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ON THE CORRELATION BETWEEN THE HEAT OF FORMATION OF CHEMICAL COMPOUNDS AND THE POSITION OF THE ELEMENTS IN THE D. I. MENDELEEV PERIODIC TABLE

V. P. Shishokin

Laury showed in 1882 that the quantity of heat which is evolved during the formation of chlorides, bromides and iodides of metals, is periodically dependent on the magnitude of the atomic weight of the elements. In 1892 Richards came to the conclusion that the heat of formation of metal fluorides is also found in periodic dependence on the atomic weight of the combined elements. In all these cases it turned out that the greatest quantity of heat is evolved by the alkaline metals. Mendeleev [1] noted that the heat of formation of oxides (according to the data of Thomsen) also conforms to a periodic dependence, the greatest magnitude however, occurs at the metals of the second group (magnesium, calcium, strontium and barium).

Thomsen himself indicated a periodic change of affinity toward oxygen in the groups of the Mendeleev table; thus, with chlorine and iodine, sulfur and tellurium, phosphorus and antimony a greater affinity toward oxygen is observed than respectively with bromine, selenium and arsenic. Biron [2] considered a detailed change in the properties of elements and their compounds, in particular - the heat of formation of compounds in the vertical direction in the Mendeleev table. It turned out that a number of properties and specifically the heat of formation of oxides changes periodically in the groups of the Mendeleev table; this phenomenon was designated by Biron as "secondary periodicity". Roth [3] in further experimental investigations confirmed the phenomenon of secondary periodicity in the change of the heat of formation of elements in the principal subgroups of the IV - VII groups; thus, the greatest heat of formation is observed in the elements of the odd periods while the least was observed in the elements of the even periods.

The work of Biron went unnoted both by Russian and by foreign investigators. Thus, A. M. Berkengeim [4,5] in his work on the connection of the heats of formation of chemical compounds with the position of the elements in the Mendeleev table did not take account of the phenomenon of secondary periodicity, which explains deviation of his calculated values from the experimental data. There was no reference to the work of Biron and Roth. Nothing is said concerning secondary periodicity in chemistry textbooks. Mendeleev himself [6] wrote in "Fundamentals of Chemistry": "...The affinity of iodine toward oxygen is much greater than that of chlorine. Bromine occupies an intermediate position".

Shchukarev and Vasilkova and Shchukarev, Ariya and Lakhtin [7, 8] showed the periodic change in the heat of formation of chemical compounds of magnesium with elements of the principal subgroups of groups IV and V of the Mendeleev table.

Kapustinsky did not take into account the phenomenon of secondary periodicity and came to an incorrect conclusion in his works on the establishment of a dependence between the heat of formation of chemical compounds and the position of elements in the Mendeleev table [9, 10].

Kapustinsky establishes the rule of "thermochemical logarithmicity", in accord with which a rectilinear relationship between the heat of formation of chemical compounds and the logarithm of the atomic number of the elements both in the periods and in the groups of the Mendeleev table should occur. However, while periodic change of the heats of formation of chemical compounds is present in the groups, the existence of thermochemical logarithmicity can not be mathematically substantiated here.

In his theoretical basis for "thermochemical logarithmicity" Kapustinsky used the representation of Yum-Rözeri concerning the reversible proportionality between the atomic radius and the cubic root of the atomic number which can not occur while there is present a graduated change in the dimensions of the atoms in the groups [11].

The straight lines presented by Kapustinsky for the dependence between the heat of formation of radicals and oxides of the elements of the principal subgroups I and II have a very small angle of inclination as a consequence of which there occurred an apparent rectification of the periodicity. In Fig. 1 the change in the heat of formation E of the chlorides of the alkaline metals is shown as a function of the changes in the logarithm of the atomic number $\log z$ of the alkaline metals on the scale of Kapustinsky (1. (figures to the right of the vertical axis), and in a greater

vertical scale (2, figures to the left of the axis). The stepwise character of the line in the second case is evidence of the manifestation of periodicity; a similar picture is observed when other examples of dependence between the heat of formation of compounds and the logarithm of the atomic number are depicted in a greater vertical scale.

For the chlorides of elements of groups III and IV and chlorides of the 2-nd, 3-rd, 4-th, and 5-th periods Kapustinsky also gave "thermochemical logarithmicities"; these straight lines were constructed on a sufficiently great scale of the heats of formation of the compounds, however the observable scattering of points is undoubtedly evidence of the presence here also of periodic change. The only verifiable example of the rule of "thermochemical logarithmicity" appears to be the rectilinear dependence existing between the logarithm of the atomic number and the heat of formation of chlorides of elements of the third period.

Kapustinsky noted that the rule of "thermochemical logarithmicity" was not applicable to the gaseous state of a substance.

In the present work an attempt is made to relate the heat of formation of chemical compounds (halides and oxides of metals) with the ionization potentials of the participating elements. Just as in the works of A. M. Berkengeim and A. F. Kapustinsky, the heat effects were taken to refer to a gram equivalent. The magnitudes of the heat effects and ionization potentials were taken from the handbook of Kei and Lebi [12].

The periodicity of the changes in the heats of formation of halides and oxides of metals in groups of the Mendeleev table is not clearly manifested. However the presence of periodicity can be shown in the change of heat effects using the processes employed by Rydberg and Bazarov to display the periodicity of the changes in the atomic weight of elements; according to the Rydberg method [1] the differences of two series of stationary quantities are compared, while according to the Bazarov method [13], the ratios of these quantities are compared.

In Tables 1 and 2 the ratios of the heats of formation of a number of significant solid halides of the alkaline metals are set forth; secondary periodicity is evident in all cases.

TABLE 1

LiF : NaF	1.01	LiCl : NaCl	0.99	LiBr : NaBr	0.97	LiI : NaI	0.94
NaF : KF	1.07	NaCl : KCl	0.94	NaBr : KBr	0.92	NaI : KI	0.88
KF : RbF	1.009	KCl : RbCl	0.993	KBr : RbBr	0.982	KI : RbI	0.973
RbF : CsF	1.011	RbCl : CsCl	0.989	RbBr : CsBr	0.981	RbI : CsI	0.966

TABLE 2

LiF : LiCl	1.49	NaF : NaCl	1.46	KF : KCl	1.29	RbF : RbCl	1.27	CsF : CsCl	1.24
LiCl : LiBr	1.16	NaCl : NaBr	1.13	KCl : KBr	1.11	RbCl : RbBr	1.09	CsCl : CsBr	1.09
LiBr : LiI	1.29	NaBr : NaI	1.25	KBr : KI	1.19	RbBr : RbI	1.18	CsBr : CsI	1.17

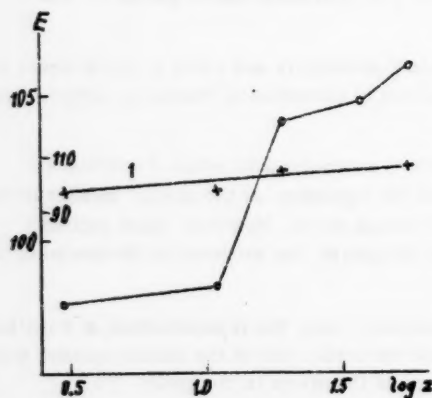


Fig. 1. Dependence between the heat of formation E of chlorides of the alkaline metals and the atomic number of the metal $\log z$. 1) On the scale of A. F. Kapustinsky; 2) at a greater vertical scale.

Fig. 2 shows that the heat of formation of the halides of the alkaline metals is linearly dependent on the square root of the magnitude of the first ionization potential of the metal; the angle of inclination of the straight lines changes stepwise in proceeding from iodides to fluorides. If with the iodides, bromides and chlorides of the alkaline metals the heats of formation are associated with a reversible dependence on the ionization potentials of the metal, with the fluorides there still occurs a straight line dependence. The greater the affinity of the halogen for electrons, the less the extent to which the ionization potential of the metal influences the heat of formation of the halide.

The heat of formation of NaF of 136 kcal (Fig. 2) set forth in the handbooks considerably

deviates from the straight line for fluorides; interpolation gives a heat of formation of NaF of 142 kcal (according to Kapustinsky, 144 kcal).

Inasmuch as both the ionization potential and the heat of formation change periodically in the groups, the existence of a rectilinear dependence between the heats of formation and the ionization potentials is possible only under definite physico-mathematical conditions.

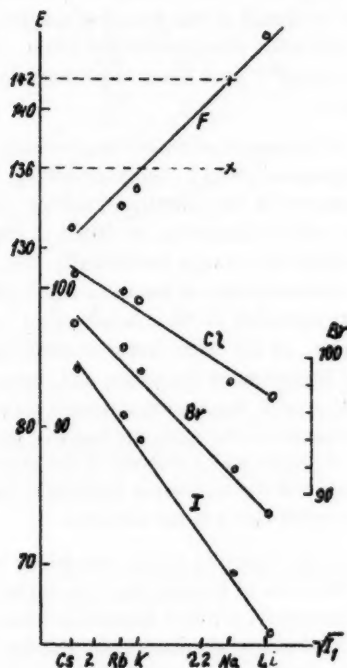


Fig. 2. Dependence between the heat of formation E of alkaline metal halides and the square root of the first ionization potential of the metal. The scale for iodides and fluorides is on the left of the axis; that for chlorides is on the right.

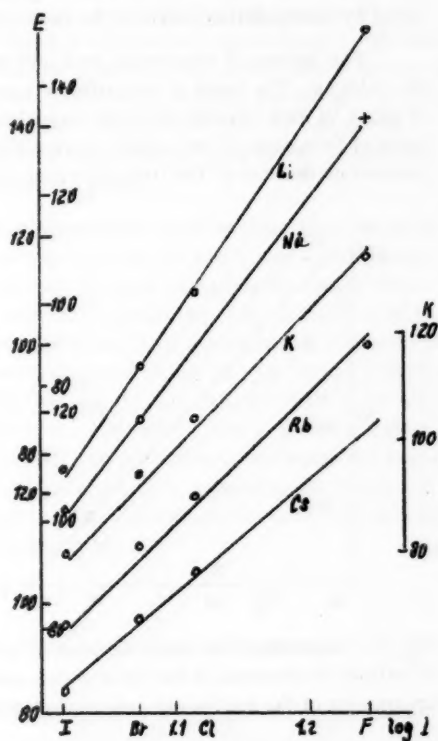


Fig. 3. Dependence between the heat of formation E of halides of the alkaline metals and the logarithm of the first ionization potential of the halogen. The scales for the halides of Cs and Na are to the left of the axis; those for the halides of Rb and Li are to the right.

It was natural to expect further that the heats of formation of the halides of the alkaline metals would be found in some dependence on the magnitudes of the affinity for electrons (null ionization potential) of the halogen. However, to demonstrate such a dependence, expressible by a simple method, was not successfully done, and it turned out that the heats of formation of the halides of the alkaline metals is associated with a rather good linear dependence on the logarithm of the first ionization potential of the halogen (Fig. 3). It is possible that errors in the determination of the electron affinity were too great (particularly with fluorine), and the first ionization potential, in general determinable with greater accuracy, can replace the null potential (the magnitudes of the latter are taken from the book of Syrkina and Dyatkina [14]).

It should be assumed in general that the heat of formation of the halide is increased with increase in the electron affinity of the halogen. The heat of formation of NaF (142 kcal) obtained by interpolation in Fig. 2, lies on the straight line for sodium (Fig. 3).

The simplest dependence between the heats of formation of the solid halides of the elements of the principal subgroup of group II and the ionization potentials of the latter turned out to be somewhat different. Specifically, these heats vary linearly with the square of the group ionization potential (the total of the first two potentials) of the metal; the heat of formation of the given halides is associated semi logarithmically, with the first potential as occurred in the preceding case.

While the heats of formation of the chlorides, bromides and iodides of the metals of the principal subgroup of group II increase smoothly with increase in the atomic number (and correspondingly with decrease in the ionization potentials), the heats of formation of the fluorides exhibited a marked scattering of the points plotted from the available data; in addition, the heat of formation of BeF_2 is completely absent. All this forced us to question the correctness of the heats of formation of fluorides indicated in the literature. Only the heat of formation of BaF_2 also fits precisely on the straight line relating the heats of formation of the metals of the principal subgroup of group II to the logarithm of the first ionization potential; the points for SrF_2 , CaF_2 and MgF_2 lie considerably above the corresponding curves. The heats of formation of SrF_2 , CaF_2 , MgF_2 and also of BeF_2 found by extrapolation proved to be respectively equal to 282, 273, 240 and 203 kcal.

The halides of aluminum, lead and antimony proved to vary linearly with the first ionization potential of the halogen. The heats of formation of compounds of aluminum with the elements of the principal subgroup of group VI vary linearly with the logarithm of the sum of the first two ionization potentials of the latter. The heats of formation of the iodides of elements of the principal subgroup of group V were found to be linearly dependent on the sum of the first three ionization potentials of these elements.

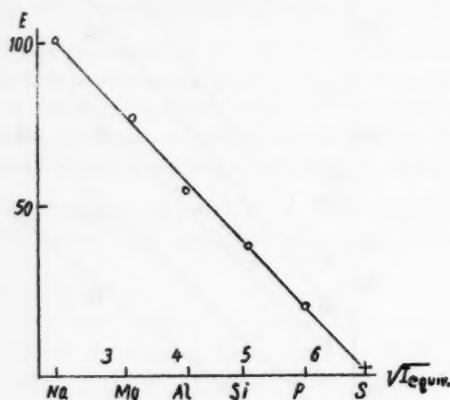


Fig. 4. Dependence between the heat of formation E of halides of elements of the third period and the square root of the equivalent potential of the element.

The heats of formation of oxides of elements of the principal subgroup of group I change smoothly; in group II there is a periodicity in the transition from Ca to Ba. In groups III–V the heats of formation of oxides of the elements of the principal subgroups change periodically; the periodicity is observed also when elements of the 2-nd and 3-rd periods are combined with elements of the side subgroups, as was done by Kapustinsky. In all cases, linear dependence between the heats of formation of the oxides and ionization potentials (as well as with the atomic number) did not appear. Linear dependence between the heats of formation of compounds of nitrogen with elements of the principal subgroup of group II and the ionization potentials (and the atomic number as well) also was not detected.

In the horizontal direction in the Mendeleev table (in the periods) the heats of formation of the oxides of the elements change smoothly; a linear dependence between the heats and the ionization potentials (and also $\log z$) is absent.

The heats of formation of chlorides in the 2-nd, 4-th and 5-th periods change periodically; there is no linear dependence between the heats and the ionization potentials (and also $\log z$). Only in the 3-rd period where the heats of formation of the chlorides change smoothly, does a linear dependence (Fig. 5) between them and the square root of the equivalent potential occur (this term is used to designate the quotient resulting from the division of the group potential by the group number).

In exactly the same way a linear dependence between the heats of formation and $\log z$ is observed for the chlorides of the elements of the 3-rd period. The heat of formation of SCl_6 determined from Fig. 4 by extrapolation amounts to 3 kcal. per 1 equiv. or 18 kcal. per 1 g-formula (Kapustinsky gives 40 kcal). In general, the heats of formation of chlorides in the periods of the Mendeleev table is associated with a reversible dependence on the equivalent potentials of the elements.

In the case of gaseous molecules there occurs a clear periodicity in the change in the heats of formation of the fluorides and partially of the chlorides of the alkaline metals; with Bazarov's method it is also manifested with the remaining halides of these metals. The iodides, bromides and chlorides exhibited the existence of a rectilinear dependence between the heats of formation and the square root of the first ionization potential of the alkaline metal, the fluorides (in particular, KF) give a certain deviation from rectilinear dependence. The linear dependence between the heats of formation of the gaseous halides of the alkaline metals and the electron affinity is also not shown, as in the case of the solid halides. Correspondingly a rectilinear dependence is apparent between the heats of formation and the logarithm of the first ionization potential.

The heats of formation of gaseous molecules of the halides of hydrogen also vary linearly with the logarithm of the first ionization potential of the halogen. Thus, in contrast to the conclusion of Kapustinsky the simplest law is observable during the formation of gaseous molecules.

The presence of a linear dependence for the chlorides of the elements of the 3-rd period between the heats of

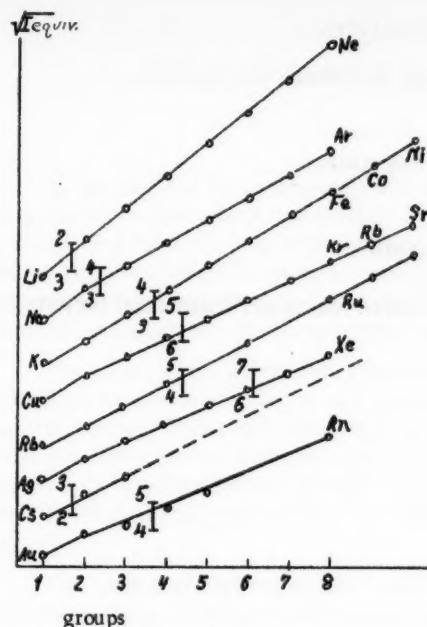


Fig. 5. Dependence between the square root of the equivalent potential and the atomic number of the element (group number)

The scale for the ordinate axis is given on the lines.

their formation, on the one hand and the square root of I_{equiv} , and $\log z$ on the other hand, still does not in itself influence the existence of a simple dependence between the equivalent potential and the atomic number. For chlorides of elements of the 2-nd, 4-th and 5-th periods a dependence between the heats of formation, on the one hand, and the square root of I_{equiv} , and $\log z$, on the other hand, is expressed by equidistant curves which also should argue in favor of the presence of the simplest dependence between I_{equiv} and z . Actually Fig. 5 shows that there exists a dependence which is very close to rectilinearity, between the atomic number and the square root of the equivalent potential (analogously to the law of Moseley); the scale for the square root of I_{equiv} is a sliding scale. It is evident that the tangent of the angle of inclination of these straight lines varies periodically in the series of the Mendeleev table.

It was found by extrapolation of the straight lines which express Moseley's law that I_1 for Co is 202 and I_9 and I_{10} for Ni are 209 and 245, and on the basis of these quantities the square roots of the corresponding equivalent potentials (Co = 9.55, Ni = 10.4); were calculated; these quantities fit on the extension of the K-Fe straight line. The points obtained in this way for Rb and Sr deviate somewhat from the Rb-Ru straight line. On the basis of the Rb-Ru straight line the magnitude of the square root of the equivalent potential of niobium (5.19) was determined, and hence the value of I_1 for this element (6.4 eV) which is lacking in the literature; the first ionization potential of niobium obtained by extrapolation by Moseley's law amounts to 6eV.

SUMMARY

1. The heats of formation of chemical compounds vary in general periodically both in the groups and in the periods of the Mendeleev table.
2. As a consequence of the presence of periodicity in the change of the heats of formation of chemical compounds the "thermochemical logarithmicity" of Kapustinsky can not be theoretically substantiated and is not practically confirmed.
3. There exists a dependence between the heats of formation of chemical compounds and the ionization potentials of the elements; the heats of formation vary inversely in dependence on the ionization potentials of the cation (oxidant) and in direct dependence on the ionization potentials of the anion (reductant). In many cases this dependence can be expressed by the simplest (linear) method. The linear dependence has a somewhat different form for various groups of compounds which is apparently due to difference in the nature of the bond in the compounds. The regularities displayed are applicable both for the gaseous and for the solid state of a substance; they permit the calculation of the heats of formation of chemical compounds which have not been determined by experimental means and the introduction of corrections in a number of the available data.
4. There exists a linear (or close to linear) dependence between the atomic number and the square root of the equivalent ionization potential of the elements.

LITERATURE CITED

- [1]. D. I. Mendeleev. Fundamentals of Chemistry (Suppl. 416), 2, 284 (1928).
- [2]. E. V. Biron, J. Russ. Chem. Soc., 47, 964 (1915).
- [3]. W. A. Roth, G. Becker, Z. phys. Chem., A, 159, 1 (1932).
- [4]. A. M. Berkengelm. Fundamentals of Theoretical Chemistry, 146 (1926).
- [5]. A. M. Berkenheim, Z. phys. Chem., A, 136, 231 (1928).
- [6]. D. I. Mendeleev. Fundamentals of Chemistry, 1, 216 (1928).
- [7]. S. A. Shchukarev, S. M. Ariya and G. I. Lakhtin, Herald of the Leningrad State University, 2, 121 (1953).

- [8]. S. A. Shchukarev and I. V. Vasilkova, *Herald of the Leningrad State University*, 2, 115 (1953).
- [9]. A. F. Kapustinsky, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1,3 (1951).
- [10] A. F. Kapustinsky and Yu. M. Golutvin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1,3,1951.
- [11] V. P. Shishokin, *J. Gen. Chem.*, 23, 889 (1953).*
- [12] Kei and Lebi, *Handbook of the Physical Experimenter*, 164, 269 (1949).
- [13] A. I. Bazarov, *J. Russ. Chem. Soc.*, 19, 61 (1887).
- [14] Ya. K. Syrkin and M. E. Dyatkina, *The Chemical Bond*, 55 (1946).

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COMPLEXES OF DIVALENT IRON WITH DIMETHYLGLYOXIME

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In the course of an investigation of a number of complex compounds of dimethylglyoxime with metals Chugaev [1,2] demonstrated that divalent iron in an alkaline medium forms a red colored compound. This reaction is widely used for the colorimetric determination of ferrous iron. However up to the present time the compound has not been isolated in the pure form and its composition has not been established. Chugaev and Orelkin [3] succeeded only in isolating a complex compound of ferrous iron with dimethyl glyoxime and pyridine $\text{Fe}(\text{HDM})_2 \cdot 2\text{Py}$; any physico-chemical characteristics of this compound were entirely lacking.

The causes of the slight study which has been devoted to this compound are associated with the experimental difficulties to overcome which proved impossible during the investigation of the complexes by the classical preparative method. These difficulties were due above all to the fact that dioxime of iron (II) is quite soluble in water and consequently could not be successfully isolated by crystallization. Further, the complex under study is formed only in alkaline medium while under these conditions ferrous iron is very rapidly oxidized in air. In addition, in the dimethylglyoxime- Fe^{++} ion system, apparently, not one, but several varied compounds (see below) are formed.

The method of physicochemical analysis of solutions of complex compounds was used in the present work for the determination of the composition and properties of the dioxime complex of divalent iron.

EXPERIMENTAL

1. Determination of the Composition of the Complex by the Isomolar Series Method. The principle of the method of determining the composition of complexes in solution according to Ostromyslensky [4] and Job [5] is based, as is well known, on the study of the optical density of series of solutions containing the reaction components in various ratios with the sum of their molar concentrations constant. The measurements of the optical density were carried out on an FM optical photometer.

Preliminary experiments established that in the presence of ammonia a compound is formed with a light absorption maximum close to $530 \text{ m}\mu$. Upon substituting pyridine for ammonia the absorption spectrum is displaced toward the short wave portion and the light absorption maximum is observed close to $496 \text{ m}\mu$.

For the study of the colored complex of ferrous dioxime, the initial solutions of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ (0.01 mole/liter) and an alcoholic solution of dimethyl glyoxime (0.01 mole per liter) were prepared. These solutions were mixed in various ratios, with their total volumes always amounting to 10 ml. To diminish the oxidation of ferrous iron, hydrazine sulfate was introduced and to prevent the precipitation of the hydrate of ferrous or ferric oxide tartaric acid was added. To prepare the solutions we used the method recommended for the colorimetric determination of ferrous iron. To x ml of 0.01 molar solution of Mohr's salt 8 ml of a saturated solution of hydrazine sulfate, 0.5 ml of 5% tartaric acid solutions and $(10 - x)$ ml of 0.01 molar alcoholic solution of dimethylglyoxime was added. The solution was heated, 5 ml of 25% ammonia was added, boiled for 30 seconds, cooled under a faucet to 19° and diluted to 25 ml with a mixture of solutions of ammonia and hydrazine (in a ratio of 1:1) or of water. Then the optical density of each of the solutions at a layer thickness of 1 mm, using the light filter indicated above, was measured.

The dependence of the optical density on the ratio of the reacting components is shown in Fig. 1. On the abscissa are plotted the quantities of ferrous iron and dimethylglyoxime in milliliters and on the ordinate — the optical density of the solutions. As is evident from the figure, the maximum light absorption of the complex is observed under the given conditions at a ratio of iron to dimethylglyoxime equal to 1:2.

2. Determination of the Composition of the Complex at Constant Concentration of One of the Components and Variable Concentration of the Other. Under the conditions of the physico-chemical analysis the series of isomolar solutions is one of the sections of the diagram of the system: central ion—coordinated ion—solvent [6]. When the complex is slightly dissociated, its composition can also be determined by other sections of the system. In particular, the sections have great significance which correspond to the following series of solutions: a) constant concentration of the central ion and variable concentration of the reagent containing the coordinated ion; b) constant concentration of the coordinated ion and variable concentration of the central ion.

These experiments are also important in order to explain whether or not one compound or several compounds of varying composition are formed in the given concentration limits. Finally, these experiments are necessary for

further investigation of the physico-chemical constants of the complex.

The compositions of all three sections can coincide only if under the given conditions the complex is rather stable, particularly, in relation to the presence of substances like reductants (hydrazine) and which form collateral complexes (tartaric acid). The rather sharp maximum of the curve in Fig. 1 shows that, apparently, the complex is slightly dissociated and weakly decomposed by the collateral substances which are present.

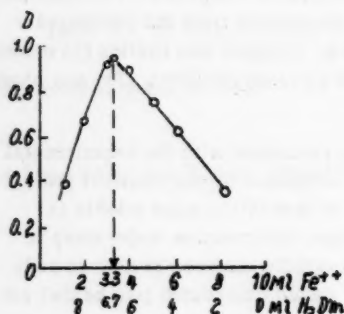


Fig. 1. Dependence of the optical density : D on the ratio of divalent iron to dimethylglyoxime.

solutions and the data of Figs. 2 and 3 that at complete association of one of the components (i.e., with excess of the other component) the following is observed. An approximately identical optical density is obtained at a concentration $[Fe^{++}] = 4 \cdot 10^{-4}$ mole (with excess dimethylglyoxime) and, on the other hand, at a concentration $[H_2Dm] = 8 \cdot 10^{-4}$ mole (at an excess of iron).

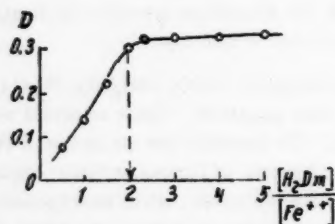


Fig. 2. Dependence of the optical density D on the dilution.

Explanation in the text

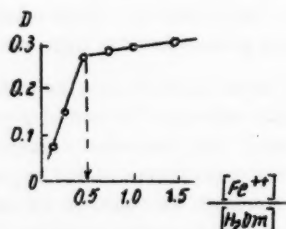


Fig. 3. Dependence of the optical density D on the dilution.

Explanation in the text.

All these data confirm that the composition of the colored complex under the given limiting conditions corresponds to a ratio of ferrous iron to dimethylglyoxime equal to 1:2. This gives a basis for considering that the composition of ferrous dioxime corresponds to the formula $Fe(HDm)_2$; thus the soluble colored complex of ferrous iron is analogous in composition to the difficultly soluble nickel compound.

3. Determination of the Dissociation Constant of the Complex. The dissociation constant of the complex characterizes its strength and is of direct significance as a basis for determining the conditions of the colorimetric determination. In addition, it was important to confirm the formula of the compound proposed above in the following respect. All the preceding experiments only make it possible to establish the ratio $Fe^{++}:H_2Dm$. However with the same ratio the formation of an addition product of a molecule of dimethylglyoxime, for example, $[Fe(H_2Dm)_2]^{++}$ or $FeX_2 \cdot 2H_2Dm$ was possible. Further, all the curves indicated above would have the same form if the composition of the complex corresponded to the formula of the disubstituted salt, for example $FeDm_2^{--}$ (or $(NH_4)_2FeDm_2$ and others.).

The study of the dependence of the equilibrium on the concentration of H^+ ions makes it possible to answer

the question raised above. If the complex has the composition $\text{Fe}(\text{HDm})_2$, then the equilibrium should be expressed by the equation



The equilibrium constant should have the form:

$$K^{\text{eq}} = \frac{[\text{Fe}(\text{HDm})_2][\text{H}^+]^2}{[\text{Fe}^{++}][\text{H}_2\text{Dm}]^2} \quad (2)$$

Evidently, in the case of the formation of an addition product of a dimethylglyoxime molecule, the equilibrium state should not depend at all on the pH of the solution. If a compound is formed where both hydrogen atoms of dimethylglyoxime are replaced, the equilibrium should depend on the fourth power of the change of concentration of H^+ ions, in accordance with the equation



It is well known [8] that the first acid dissociation constant of dimethylglyoxime is equal to $8 \cdot 10^{-12}$; consequently, in a solution with a pH less than 10, dimethylglyoxime is found almost entirely in the form of the H_2Dm molecule.

In connection with what has been said a number of experiments were set up to determine the equilibrium constants at various pH values of the solution. To obtain well measurable results it was necessary to set up the experiments under conditions in which increase in the concentration of hydrogen ions caused appreciable diminution in the optical density of the solution. It was preliminarily established that this is observed at a pH of about 6.5-8. At pH approximately equal to 7 and at greater concentrations of Fe^{++} ions it is possible to partially precipitate the hydrate of ferrous oxide [7]. The use of any compound which forms a complex (as tartaric acid, etc.) is inconvenient, since in this case, evidently, the equilibrium concentration of free Fe^{++} ions will be considerably less than the total concentration of ferrous iron not bound to dimethylglyoxime. The latter circumstance does not interfere with the explanation of the question raised above concerning the composition of the dioxime, since for this purpose it was necessary to measure only the degree of displacement of the equilibrium at changing pH of the solution. However, it was impossible to set up the direct calculation from these same data of the numerical values of the instability constants of ferrous dioxime.

Experiment showed that in dilute solutions at Fe^{++} concentrations of the order of 10^{-4} - 10^{-5} mole in the presence of a sufficient excess of dimethylglyoxime, it is not necessary to introduce tartaric acid, since under these conditions a precipitate of $\text{Fe}(\text{OH})_2$ is not formed. It is true that rather rapid oxidation in air is observed; consequently the measurement of the optical density was carried out by us as rapidly as possible after the preparation of each solution. In addition, hydrazine sulfate, the solution of which was preliminarily brought by addition of alkali to the necessary pH value, was introduced into the solution. This solution plays the role of a buffer and at the same time reduces the oxidation of ferrous iron. In order to diminish the influence of oxidation of the iron by air, it was convenient to work with as concentrated as possible solutions of the complex. In view of the intense coloration of such solutions the optical density was measured with layers of small thickness.

The solutions for measuring the optical density were prepared in the following manner. To 10 ml of previously prepared solution, containing hydrazine sulfate and alkali, 1 ml of a solution of Mohr's salt (10^{-2} mole per liter) and 1 ml of 0.1 molar alcoholic dimethylglyoxime solution were added. The optical density of the colored solution obtained was measured with a light filter with an effective wave length of 533 m μ , at a layer thickness of 1 mm. In a separate test sample, containing 10 ml of buffer solution and 1 ml of Mohr salt (i.e., without dimethylglyoxime), the pH was verified by a colorimetric method (with a two color indicator). The results of the measurements of optical density at various pH values of the solution are set forth in the table.

Taking into account the conditions of the experiments and the possible errors (in particular the partial oxidation of Fe^{++}), we utilized the following method of treating the results. At a pH approximately equal to 7.7 it can be assumed that the iron is completely bound in the colored complex; consequently the ratio of the optical density in each separate experiment (D_n) to the optical density $D = 0.65$ gives the ratio of the concentrations $[\text{Fe}_{\text{complex}}] / [\text{Fe}_{\text{total}}]$. These data are set forth in column 3 of the table. Knowing both concentrations ($[\text{Fe}_{\text{complex}}]$ and $[\text{Fe}_{\text{total}}]$) we can calculate (by differences) the concentration of the Fe^{++} ions which are not bound in the complex and find the ratio of the concentrations of the complex-bound and unbound iron, i.e., $[\text{Fe}(\text{HDm})_2] / [\text{Fe}^{++}]$. These ratios are set forth in column 4 in the form of their logarithms.

Expressing the constants of equation (2) logarithmically, we obtain:

$$\log K^{\text{eq}} = 2 \log [\text{H}^+] + \log \frac{[\text{Fe}(\text{HDm})_2]}{[\text{Fe}^{++}]} - 2 \log [\text{H}_2\text{Dm}] \quad (4)$$

Keeping in view that in all the solutions there was a sufficient excess of free dimethylglyoxime, we can cal-

culate the constant concentration $[H_2Dm]$ and transform equation (4) in the following manner:

$$\log \frac{[Fe(HDm)_2]}{[Fe^{++}]} = 2pH + \text{const.} \quad (5)$$

This relationship should be expressible by a straight line; if on the graph identical scales for $\log [Fe(HDm)_2]/[Fe^{++}]$ and for pH are taken, then, evidently, the tangent of the angle of inclination of the straight line will be equal to the coefficient at the pH, i.e. must be $\tan \alpha = 2$. In this case, if the reaction were proceeding in accord with equation (3), $\tan \alpha$ would be equal to 4.

TABLE

pH	Optical density	$\frac{[Fe_{\text{complex}}]}{[Fe_{\text{total}}]}$	$\log \frac{[Fe_{\text{bound}}]}{[Fe_{\text{free}}]}$	$K'_{\text{equil.}} = \frac{[FeHDm^+][H^+]}{[Fe^{++}][H_2Dm]}$	$K''_{\text{equil.}} = \frac{[Fe(HDm)_2][H^+]^2}{[Fe^{++}][H_2Dm]^2}$
5.6	0.04	0.06	-1.19	$1.93 \cdot 10^{-5}$	$(5.85 \cdot 10^{-9})$
5.8	0.05	0.08	-1.06	$1.66 \cdot 10^{-5}$	$(3.17 \cdot 10^{-9})$
6.0	0.08	0.12	-0.86	$1.64 \cdot 10^{-5}$	$(1.98 \cdot 10^{-9})$
6.2	0.12	0.18	-0.66	$1.67 \cdot 10^{-5}$	$(1.01 \cdot 10^{-9})$
6.5	0.15	0.23	-0.52	$(1.14 \cdot 10^{-5})$	$0.43 \cdot 10^{-9}$
6.7	0.28	0.43	-0.12	$(1.81 \cdot 10^{-5})$	$0.44 \cdot 10^{-9}$
6.9	0.37	0.57	0.12	$(2.01 \cdot 10^{-5})$	$0.31 \cdot 10^{-9}$
7.1	0.50	0.77	0.52	$(3.20 \cdot 10^{-5})$	$0.31 \cdot 10^{-9}$
7.3	0.57	0.87	0.82	$(4.04 \cdot 10^{-5})$	$0.24 \cdot 10^{-9}$
7.4	0.60	0.92	1.06	$(5.52 \cdot 10^{-5})$	$0.26 \cdot 10^{-9}$
7.5	0.62	0.95	1.27	$(7.24 \cdot 10^{-5})$	$0.27 \cdot 10^{-9}$
7.7	0.65	1.00	—	—	—
7.9	0.65	1.00	—	—	—

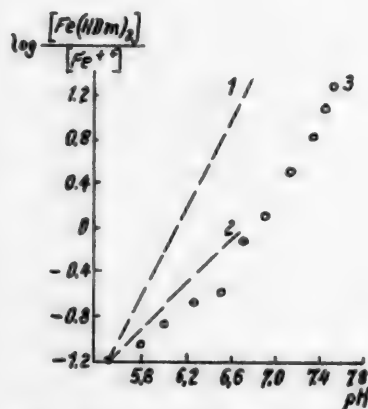


Fig. 4. Dependence of the logarithm of the ratio of the concentrations of complex bound and unbound iron on the pH.

1) $\tan \alpha = 2$; 2) $\tan \alpha = 1$; 3) experimental data.

of equation (2) (column 6 of the table), prove to be variable at pH values from 5.6 to 6.2 (these values are placed in parentheses in the table); however at $pH > 6.2$ the values of $K''_{\text{equil.}}$ become constant; In connection with what has been said during the calculation of the average value $K''_{\text{equil.}}$ [in accord with equation (1)] attention is paid only to the values obtained in the pH range from 6.5 to 7.5.

$$K''_{\text{equil.}} = \frac{[Fe(HDm)_2][H^+]^2}{[Fe^{++}][H_2Dm]^2} = 0.32 \cdot 10^{-9} \quad (6)$$

The first acid dissociation constant of dimethylglyoxime [8] is equal to $K_{H_2Dm} = \frac{[H^+][HDm^-]}{[H_2Dm]} = 8 \cdot 10^{-12}$.

In Fig. 4 the results obtained on the basis of the experiments considered in the table are noted by the points. As is evident, the points do not fit on a single straight line, which suggests the presence in the system, in addition to $Fe(HDm)_2$, of still other complex compounds. But beginning at a pH approximately equal to 6.5 and higher the points almost fit on a straight line, the tangent of the angle of inclination of which, $\tan \alpha = 2$. A dependence which corresponds to $\tan \alpha = 4$ is not found in any pH range; thus, the hypothesis to the effect that the reaction at the given pH can proceed in accord with equation (3) must be rejected. In exactly the same way, evidently there is no basis for assuming the formation of a product of the addition of the dimethylglyoxime molecule. According to the data of Fig. 4 it is evident that up to pH 6.2–6.5 the inclination of the curve corresponds to the coefficient at H^+ equal to 1. The results of the calculations set forth in column 6 of the table, confirm these conclusions. Actually, the calculated value of the equilibrium constant $K'_{\text{equil.}} = \frac{[FeHDm^+][H^+]}{[Fe^{++}][H_2Dm]}$ proves to be rather constant in the pH range from 5.6 to 6.2. After this the value of the constant begins to significantly change (the corresponding values are placed in parentheses), since the equilibrium ceases to correspond with equation (8). On the other hand, the values of the constant, calculated on the basis

Comparing the expression for the constant of equation (2) with the first acid dissociation constant of dimethylglyoxime and the instability constant of the complex $K_{\text{complex}} = \frac{[\text{Fe}^{++}][\text{HDm}^-]^2}{[\text{Fe}(\text{HDm})_2]}$ we obtain: $K_{\text{equil.}} = \frac{K_{\text{H}_2\text{Dm}}^2}{K_{\text{complex}}}$. From this the value of the instability constant of the complex of divalent iron with dimethylglyoxime can be calculated:

$$K_{\text{complex}} = \frac{[\text{Fe}^{++}][\text{HDm}^-]^2}{[\text{Fe}(\text{HDm})_2]} = \frac{(8 \cdot 10^{-12})^2}{0.32 \cdot 10^{-8}} = 2.0 \cdot 10^{-15} \quad (7)$$

4. Other Complexes in the System Fe^{++} - Dimethylglyoxime in Solution. During the reaction of the central ion with the coordinated ion in solution, depending on the concentration conditions, there are ordinarily formed several complex groups of varying composition. A more detailed investigation of the system Fe^{++} - dimethylglyoxime showed that the complex $\text{Fe}(\text{HDm})_2$ described above, although it appeared predominant over a rather wide range of concentrations, none the less is not the sole compound in this system. Omitting the experimental details, a number of data can be adduced which indicate the formation of other complex groups which differ from that described above in the ratio $\text{Fe}^{++} : \text{H}_2\text{Dm}$ and in stability.

During the study of the equilibrium formation of the complex at various pH values it could be shown (Fig. 4), that in more acidic medium (pH approximately equal to 5.4-6.5) the value of $\tan \alpha$ is approximately equal to 1. This means that in this portion of the concentration conditions the equilibrium of the reaction between Fe^{++} and H_2Dm depends on the first power on the concentration of H^+ ions. In this range of conditions it is most probable to consider the reaction to be



(The corresponding values of $K_{\text{equil.}}$ are shown in column 5 of the table).

The formation of a similar complex group $(\text{FeHDm})^+$ is confirmed by a number of other data. Thus, the series of isomolar solutions at very low concentrations of the reacting components gives results which differ from the curve of Fig. 1; under these conditions displacement of the maximum in the direction of the ratio $\text{Fe}^{++} : \text{H}_2\text{Dm} = 1:1$ is observed. It is true that in strongly diluted solutions it is difficult to eliminate the influence of the oxygen of the air; consequently we carried out several additional experiments. The colored complex formed in the system $\text{Fe}-\text{H}_2\text{Dm}$ was partially extracted with several organic solvents; it was thereupon observed that, if an excess of Fe^{++} ions was introduced into the aqueous phase, then the color of the extract was appreciably different from the color of the extract obtained with excess dimethylglyoxime. Finally, during the electrolysis of an aqueous solution containing excess Fe^{++} (relative to the dimethylglyoxime), the movement of the colored layer to the cathode is observed. With excess Fe^{++} , it is evident, the following reaction occurs:



In addition to the $(\text{FeHDm})^+$ complex described above [along with $\text{Fe}(\text{HDm})_2$], at least one additional complex is also formed in strongly alkaline medium with excess dimethylglyoxime anions. This is confirmed by the following data. As was shown above, the colored complex $\text{Fe}(\text{HDm})_2$ is formed only at pH approximately equal to 7 while a complex analogous in composition to the difficultly soluble nickel complex is also formed in a more acid medium. This indicates that the energy of the chemical bond between Ni^{++} and HDm^- ions is considerably greater than the energy of the chemical bond between the Fe^{++} and HDm^- ions. Thus, the equilibrium



must be strongly displaced to the right. The constant of this equilibrium must be equal to:

$$K_{\text{equil.}} = \frac{[\text{Fe}^{++}]}{[\text{Ni}^{++}][\text{Fe}(\text{HDm})_2]} = \frac{K_{\text{complex}}}{K_s(\text{Ni}(\text{HDm})_2)} \quad (11)$$

The solubility product of nickel dioxime is equal to:

$$K_s(\text{Ni}(\text{HDm})_2) = [\text{Ni}^{++}][\text{HDm}^-]^2 = 2 \cdot 10^{-15}$$

Placing the value of K_s and K_{complex} in equation (11), we obtain:

$$K_{\text{equil.}} = \frac{K_{\text{complex}}}{K_s(\text{Ni}(\text{HDm})_2)} = \frac{2 \cdot 10^{-15}}{2 \cdot 10^{-15}} = 1 \cdot 10^0$$

This quantity shows that equilibrium (10) must be almost completely displaced to the right. Actually, if nickel salt is added to a weakly alkaline solution (pH approximately equal to 8) of $\text{Fe}(\text{HDm})_2$, a red precipitate of nickel dioxime is at once formed. This precipitate is excellently extracted by chloroform, and the aqueous phase is completely decolorized. This confirms the conclusion set forth above. However, if a similar experiment is performed at a greater excess of NH_4OH , then the precipitate of nickel dioxime is not formed. By shaking such a solution with chloroform, absolutely no extraction of nickel dioxime is observed.

On the basis of the latter data, by analogy with other complexes of metals with weakly monobasic acids, and also by analogy with the Cu^{++} - dimethylglyoxime system [9], the formation of complexes of disubstituted salts can be assumed according to the following reaction:



or



It is well known that the precipitate of nickel dioxime is dissolved in caustic alkalis which, apparently, is associated with the formation of a similar di-substituted compound of dimethylglyoxime NiDm_2^{--} [10]. However as a consequence of the very small solubility of nickel dioxime $\text{Ni}(\text{HDm})_2$ a similar process takes place for it only with excess caustic alkali. At the same time, for the quite soluble $\text{Fe}(\text{HDm})_2$ complex a similar process must occur considerably earlier, i.e., at a smaller excess of OH ions.

The very energetic oxidation of Fe^{++} in strongly alkaline solutions extraordinarily complicates the more exact investigation of the equilibrium and composition of the complexes being formed. None the less, the experiments set forth show the formation of ferrous dioxime to be stronger than nickel dioxime.

SUMMARY

The method of physico-chemical analysis of solutions was utilized for the study of the colored complex of the dioxime of divalent iron. The optical density was measured as a property of the system. It was found by the method of isomolar series and by other sections of the $\text{Fe}^{++} - \text{H}_2\text{Dm} \rightleftharpoons \text{H}_2\text{Dm}$ system that the composition of the complex at pH approximately equal to 6.5-8 corresponds to a ratio of $\text{Fe}^{++} : \text{H}_2\text{Dm}$ equal to 1:2.

The dependence of the equilibrium of the reaction on the concentration of H^+ ions was studied. On the basis of these data the instability constant of the complex was calculated:

$$K_{\text{complex}} = \frac{[\text{Fe}^{++}][\text{HDm}]^2}{[\text{Fe}(\text{HDm})_2]} = \frac{(8 \cdot 10^{-12})^2}{0.32 \cdot 10^{-9}} = 2 \cdot 10^{-13}$$

It was shown that in more acid medium, and also with excess Fe^{++} , another complex group is formed; it is most probable that this is FeHDm^+ .

In more alkaline medium with excess dimethylglyoxime anions a more stable complex is formed in which iron replaces 2 hydrogen atoms of the dimethylglyoxime.

LITERATURE CITED

- [1]. L. A. Chugaev, J. Russ. Chem. Soc., 41, 1, 184 (1909).
- [2]. L. A. Chugaev, J. Russ. Chem. Soc., 31, 1 243 (1905).
- [3]. L. A. Chugaev and B. P. Orelkin, J. Russ. Chem. Soc. 46, 2, 1874 (1914).
- [4]. L. I. Ostromyslensky, Ber., 44, 268 (1911).
- [5]. P. Job, Ann. Chim., 9, 113 (1928).
- [6]. A. K. Babko, J. Gen. Chem., 18, 816 (1948).
- [7]. I. M. Kolthoff and V. A. Stenger, Volumetric Analysis, V. 2, State Chem. Press., p. 223 (1952).
- [8]. A. K. Babko and P. B. Mikhelson, J. Anal. Chem., 6, 5, 268 (1951).
- [9]. A. K. Babko and M. V. Korotun, J. Gen. Chem., 23, 8, 1302 (1953). **
- [10]. K. B. Yatsimirsky and Z. M. Grafova, J. Gen Chem., 23, 6, 935 (1953).

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* Ferrous dioximin is not extracted under these conditions.

** See Consultants Bureau Translation, p. 973.

SOLUBILITY IN THE WATER-ETHYL ALCOHOL-AMMONIUM DIFLUORIDE SYSTEM AT 25°

A. K. Zhdanov and M. A. Sarkazov

In connection with the question of the optimal composition of water-alcohol mixtures for washing precipitates of binary and complex fluorides one of us [1] undertook the study of the equilibria in the ternary system water-ethylalcohol-sodium fluoride and showed that the solubility of sodium fluoride is diminished with increasing quantity of alcohol in the mixture. The results of the study of the equilibria in the system water-ethyl alcohol-ammonium difluoride at 25° are presented in the present communication.

Binary System Ammonium Difluoride - Water. The solubility of ammonium difluoride in water at various temperatures was studied by Spitsin, Sokolova, Popova and Zaring [2] and later by Yaltov and Polyakova [3]. The first investigators [2] determined the solubility of ammonium difluoride in 1 and 5% aqueous solutions of hydrofluoric acid at -20, -10, 0, 10, 20 and 50°. The second group of investigators [3] determined the solubility of ammonium difluoride in water at 0, 10, 20, 40, 60, 80 and 100°. They established that the solid phase at all temperatures in the binary system consisted of the anhydrous salt.

EXPERIMENTAL

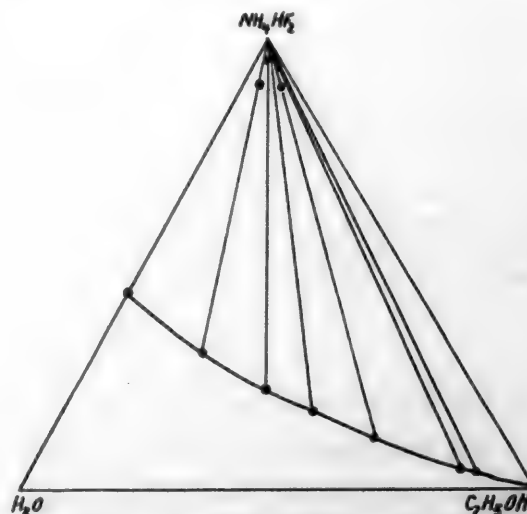
Reagents. In the course of carrying out the present investigation we used reagents of a rather high degree of purity. Kahlbaum brand ammonium difluoride was used; alcohol rectificate was subjected to fractional distillation and its content in the distillate was established via measurement of the density. The solutions of other substances which we used for the analysis of the solutions and moist precipitates, as, for example, potassium dichromate, sodium thiosulfate, alkalis and acids, were prepared from chemically pure brand reagents. The water was twice redistilled.

With the object of determining the solubility of ammonium difluoride in water at 25° and verifying the literature data, experiments were set up involving the determination of the solubility of this salt in water at 0, 25, 40 and 50° in a paraffined vessel. The values for the solubility of ammonium difluoride in water were calculated from the results of the analysis of the saturated solution for content of ammonium and fluorine.

In Table 1 along with our data for the solubility of ammonium difluoride in water at 0, 20, 40 and 60° are presented the data obtained by Yaltov and Polyakova [3].

TABLE 1
Solubility of Ammonium Difluoride in Water

Solubility (in % by weight)		Temperature
According to V.S. Yaltov and E.M. Polyakova	Our Data	
28.45	32.87	0°
37.56	—	20
—	43.73	25
50.05	53.03	40
—	54.15	50
61.00	—	60



Equilibrium in the water-ethyl alcohol-ammonium difluoride system at 25°.

It is evident from the data of Table 1 that the values obtained by us for the solubility of ammonium difluoride for 0 and 40° are higher than those of Yaltov and Polyakova [3]. As the ammonium difluoride used by us was of a high degree of purity, we are inclined to think that the low values for solubility of the difluoride obtained by Yaltov and Polyakova were due to the insufficient purity of the ammonium difluoride.

Preparation of Saturated Solutions of Ammonium Difluoride

The preparation of the saturated solutions of ammonium difluoride mixtures was carried out in a special vessel with a mercury seal. The study of the equilibria was begun with solutions containing a large quantity of alcohol and solid ammonium difluoride. The increase in the content of water in the mixture was achieved by introducing into the vessel a definite quantity of bidistillate. Such a procedure for the study of the equilibria in the system was due to the fact that in the presence of alcohol fluorides have practically no action on glass. The quantity of water introduced into the vessel to prepare the saturated solutions of difluoride was calculated on the basis of the analytical data of the preceding test solution so that a solution with the assigned content of alcohol would be obtained.

The mixture was subjected to thermostating with constant intensive stirring for a duration of 6-8 hours, after which the solution in the vessel was let stand at the same temperature and the removal of a sample of the solution and the ground phase was carried out.

It was established by special experiments that the equilibrium in the system was reached after 4-5 hours of continuous stirring, and consequently subsequently the stirring for all samples was carried out for 6-8 hours.

At the same time that samples of the solution were removed for analysis, a sample of the solution was removed in a pycnometer to determine the density and also a sample of the moist precipitate to determine the composition of the solid phase by the residue method.

Methods of Analysis of the Solutions and Moist Precipitates. The solutions and moist precipitates were analyzed for their content of ethyl alcohol and ammonium difluoride. The content of water was determined by differences.

The determination of the alcohol content in the samples taken for analysis as well as of the solid phase was carried out by the iodometric method as in the preceding work [1]. The content of ammonium difluoride for the majority of samples was found by determination of ammonium and fluorine. For a small number of samples only, the ammonium was determined by a direct (distillation) method based on the titration with a standard solution of alkali of the excess of 0.1 N acid introduced which was left after absorption of the ammonia evolved from the sample under the action of alkali. The content of fluorine in the samples taken was determined by a modified Stark method [1].

DISCUSSION OF RESULTS

The results obtained by us for the determinations of the solubility of ammonium difluoride in water-alcohol mixtures of varying composition are presented by us in Table 2 and depicted graphically in the figure in the form of a Gibbs triangular diagram.

As is evident from the data of Table 2 and the figure, the solubility of ammonium difluoride in water-alcohol mixtures of varying composition is diminished with increasing quantity of alcohol in the mixture and reaches 1.73% by weight in a water-alcohol mixture containing about 90% alcohol, in place of 42.73% by weight in pure water.

It is evident from consideration of the triangular Gibbs diagram that all conoids of composition of the solution - composition of the precipitate converge in the corner of the diagram corresponding to 100% of ammonium difluoride. It can therefore be considered that the solid phase in the water - ethyl alcohol - ammonium difluoride system consists of anhydrous ammonium difluoride.

SUMMARY

1. The solubility in the system water - ethyl alcohol - ammonium difluoride at 25° was determined.
2. The determination of the solubility of ammonium difluoride in water at 0, 25, 40 and 50° was carried out.
3. It was established that the solid phase in the ternary system water - ethyl alcohol - ammonium difluoride at 25° consists of anhydrous ammonium difluoride.

TABLE 2

Equilibria in the Water-Ethyl Alcohol-Ammonium Difluoride System at 25°

Density of the solution (g/ml)	Composition of the solution (in % by weight)			Composition of the moist precipitate (in % by weight)			Ground phase
	Alcohol	Ammonium difluoride	Water	Alcohol	Ammonium difluoride	Water	
0.8118	88.21	1.73	10.06	0.60	95.13	4.27	NH ₄ HF ₂
0.8302	84.80	2.95	12.25	0.53	93.62	5.85	
0.8514	75.90	5.02	19.08	0.52	95.41	4.07	
0.8716	73.24	6.53	20.23	0.99	94.88	4.13	
0.8979	63.97	11.17	24.86	5.57	90.34	4.09	
0.9395	49.69	16.53	33.78	1.95	90.63	7.42	
0.9813	37.55	22.19	40.26	1.95	95.03	13.02	
—	27.69	28.45	43.86	—	—	—	
—	21.47	30.47	48.06	1.45	96.82	1.73	
—	0.83	38.97	60.20	—	—	—	
—	—	43.73	56.27	—	—	—	

4. It was established that the solubility of ammonium difluoride in water-alcohol mixtures diminishes with increasing content of alcohol in the mixture and reaches at 25° a value of 1.73% by weight in the presence of 90% alcohol instead of 43.73% by weight in pure water.

LITERATURE CITED

- [1] A. K. Zhdanov, J. Gen. Chem., 24, 766 (1954).*
- [2] N. I. Spitsin, G. V. Sokolova, T. P. Popova and I. I. Zaring, J. Chem. Indust., 3, 50 (1933).
- [3] V. S. Yaltov and E. M. Polyakova, J. Gen. Chem., 15, 724 (1945).

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* See Consultants Bureau Translation, p. 773.



SOLUBILITY IN THE SYSTEM WATER - ETHYL ALCOHOL -

SODIUM FLUORIDE AT 0 AND 25°

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It has been noted for some time now that the solubility of many inorganic compounds in water is markedly diminished by addition of organic solvents, for example of alcohols, ketones and certain other substances. This phenomenon has served as the basis for the utilization of organic solvents in chemical analysis. The separation of a whole series of salts is based on the differential solubility of them in various solvents [1 - 5].

In a number of cases water-alcohol mixtures find application in chemical analysis for washing precipitates which are appreciably soluble in water, with the object of washing them free from excess precipitant and other salts found in the mother liquor and included in the precipitate. The best conditions for washing a precipitate must be considered such that the alcohol-water mixture employed to wash the precipitate hardly dissolves the precipitate but significantly dissolves the excess precipitant and other salts included in the mother liquor. It should be noted that in the question of the composition of the water-alcoholic mixtures which should be used to wash precipitates, empiricism is the rule and, in particular, literature data on the solubility of the fluorides of the alkaline metals, which are used as precipitants in photometric methods of analysis, are absent; consequently it is of interest to study the equilibria in the system water - ethyl alcohol - sodium fluoride and on the basis of the results obtained to proceed to the solution of the problem concerning the optimal composition of water-alcohol mixtures for washing the precipitates of binary and complex fluorides.

EXPERIMENTAL

Preparation of the Reagents. Sodium fluoride was prepared by neutralizing pure hydrofluoric acid with a solution of sodium hydroxide with phenolphthalein as the indicator with subsequent concentration of the sodium fluoride solution almost to dryness on an air bath. The precipitate which settled out was filtered through a porous filter, washed with bidistillate to the disappearance of the rose color, transferred into a platinum dish and dried in a drying chamber at 150°.

The alcohol rectificate was subjected to redistillation. The content of alcohol in the distillate was established by density measurements with the aid of a pycnometer at 25°.

The solutions of other substances necessary for carrying out the present investigation were prepared from chemically pure reagents. Certain of the reagents were additionally purified by recrystallization from bidistillate.

The water was twice redistilled.

Determination of the Solubility. The solubility in the system water - ethyl alcohol - sodium fluoride was determined at 0 and 25°.

The preparation of saturated solutions of sodium fluoride in water-alcohol mixtures was carried out in a special apparatus with a mercury seal.

The water-alcohol mixtures with varying compositions were prepared preliminarily in conical flasks with ground stoppers by mixing weighed quantities of water and alcohol. In all the flasks dry sodium fluoride was introduced in a quantity exceeding the magnitude of its solubility in water to obtain a saturated solution. The thus prepared solutions were kept for a prolonged time (1.5 - 2 months) at room temperature, with periodic shaking and then were transferred into an apparatus for the determination of the solubility and thermostated at constant intensive stirring for a duration of 6-8 hours, after which the removal of samples of the solution was carried out at the same temperature with a special pipet with a filtration glass plate sealed in it. In several cases samples of the ground phase were removed in preliminarily weighed containers.

Methods of Analysis of the Solutions and Moist Precipitates. The samples of the solution and ground phase taken were analyzed for content in them of ethyl alcohol and sodium fluoride. The content of water was determined by differences. To determine the content of sodium fluoride in the solution a weighed quantity of it was placed in a preliminarily weighed platinum dish and the concentration of the solution was carried out on a water bath to dryness and maintained in a drying chamber to constant weight at 150°.

The determination of the content of alcohol in the solution and the ground phase was carried out by an iodometric method based on the oxidation of ethyl alcohol in acidic medium by potassium bichromate to acetic acid and subsequent titration of the iodine evolved with thiosulfate.

The sodium fluoride in the ground phase was determined by analysis of the sample taken for fluorine by a modification of the Stark method; the fluorine was precipitated in the form of lead fluorochloride, the precipitate filtered off, washed and dissolved in nitric acid. The chloride ion evolved from the precipitate was titrated with 0.1 N AgNO_3 potentiometrically with a silver indicator electrode.

DISCUSSION OF RESULTS

The results obtained by us of the determinations for the solubility of sodium fluoride in water-alcohol mixtures of various compositions are presented in Tables 1 and 2 and depicted for 25° graphically (Fig. 1) on a Gibbs triangular diagram and on a rectangular diagram for the dependence of solubility of sodium fluoride on the concentration of alcohol in the mixture (Fig. 2).

As is evident from Fig. 1, all the conoids of composition of the solution-composition of the precipitate practically converge at the corner of the diagram corresponding to 100% NaF; it can consequently be considered that the solid phase in the system water - ethyl alcohol - sodium fluoride is anhydrous sodium fluoride.

TABLE 1

Equilibrium in the Water - Ethyl Alcohol - Sodium Fluoride System at 0°.

Density of the solution (g/ml)	Composition of the solution (% by weight)			Composition of the moist precipitate (% by weight)			Ground phase
	H_2O	$\text{C}_2\text{H}_5\text{OH}$	NaF	H_2O	$\text{C}_2\text{H}_5\text{OH}$	NaF	
1.0893	96.37	—	3.63	—	—	—	NaF
1.0871	88.10	9.70	2.20	—	—	—	
0.9880	77.89	20.88	1.23	23.23	5.63	71.14	
0.9706	69.50	29.80	0.70	—	—	—	
0.9523	59.00	40.60	0.40	14.06	10.44	75.50	
0.9258	46.48	53.26	0.26	—	—	—	
0.9018	38.67	61.30	0.03	13.40	8.18	78.42	
0.8623	18.60	81.38	0.02	—	—	—	

TABLE 2

Equilibrium in the Water - Ethyl Alcohol - Sodium Fluoride System at 25°

Density of the solution (g/ml)	Composition of the solution (% by weight)			Composition of the moist precipitate (% by weight)			Ground phase
	H_2O	$\text{C}_2\text{H}_5\text{OH}$	NaF	H_2O	$\text{C}_2\text{H}_5\text{OH}$	NaF	
1.038	96.15	—	3.85	—	—	—	NaF
1.007	87.48	10.11	2.41	29.14	4.34	66.52	
0.9798	77.81	20.81	1.38	22.53	7.44	70.03	
0.9572	71.04	28.31	0.65	26.31	10.50	63.19	
0.9312	57.13	42.47	0.40	—	—	—	
0.9131	42.05	50.54	0.31	16.22	17.64	66.14	
0.8912	40.15	59.71	0.14	—	—	—	
0.8764	32.28	67.64	0.08	10.43	25.36	64.21	
0.8446	27.63	72.33	0.04	—	—	—	
0.8175	17.44	82.54	0.02	—	—	—	

As is evident from Fig. 2, the solubility curve of sodium fluoride in water-alcohol mixtures initially falls steeply to an approximate content of alcohol in the mixture of 40-50% by weight. Upon further increase in the content of alcohol in the mixture the angle of inclination of the curve is less and the curve itself proceeds more smoothly, showing that the solubility of sodium fluoride in the presence of such quantities of alcohol is practically slightly

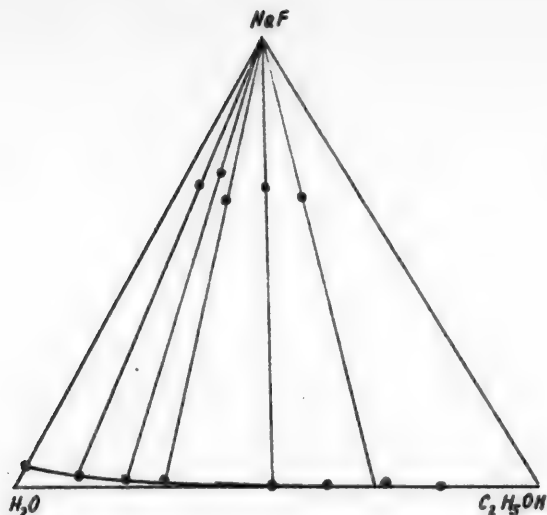


Fig. 1. Equilibria in the water - ethyl alcohol - sodium fluoride system at 25°.

mixtures containing 45-50% alcohol should be used if the washing is carried out with cooled mixture and 50-60% at temperatures significantly above 0°. To use water-alcohol mixtures with a greater content of alcohol for washing the precipitates is inadvisable since, in view of the insignificant solubility of sodium fluoride and other salts in strong water-alcohol mixtures, not all the admixture will be washed off. The density of the solutions of sodium fluoride in water-alcohol mixtures is diminished with increase in the percentage content of alcohol in the mixture. Since the solubility of sodium fluoride in water is small while it becomes still less in water-alcohol mixtures, the change in density of the solutions in the given ternary system is in accord with its change in the binary system water-alcohol.

SUMMARY

1. The solubilities of sodium fluoride at 0 and 25° were determined in the system water - ethyl alcohol - sodium fluoride.
2. It was established that the solid phase in the ternary system water - ethyl alcohol - sodium fluoride at 0 and 25° is sodium fluoride.
3. It was established that the solubility of sodium fluoride in water-alcohol mixtures diminishes with increasing alcohol content.
4. Since the solubility of sodium fluoride in water-alcohol mixtures containing more than 50% of alcohol is very small and practically is slightly changed upon further increase in the concentration of alcohol in the mixture, to wash precipitates of binary and complex fluorides free from excess sodium fluoride and other admixtures a water-alcohol mixture containing 50-60% of alcohol should be used.

LITERATURE CITED

- [1] V. F. Gillebrand and G. E. Lendel. Practical Manual on Inorganic Analysis. United Sci. Tech. Press, Moscow, p. 527-530, 560-573 (1935).
- [2] I. M. Kolthoff and E. B. Sendel. Quantitative Analysis. State Chem. Press., Moscow-Leningrad, p. 92, 429, 435 (1948).
- [3] Streibinger and Holzer, Z. anal. Chem., 90, 81 (1932).
- [4] Smith and Shead, J. Am. Chem. Soc., 54, 1722 (1932).
- [5] S. D. Beskov and O. A. Slizkovskaya, Sci. Rep., V. I. Lenin Moscow State Pedagogic Institute, 4, 15, 51, 58 (1947).

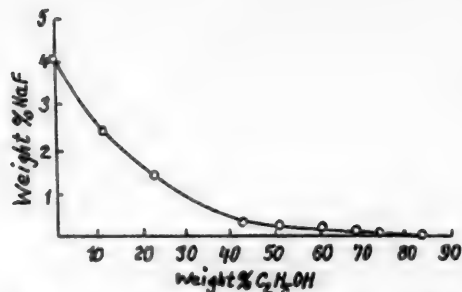
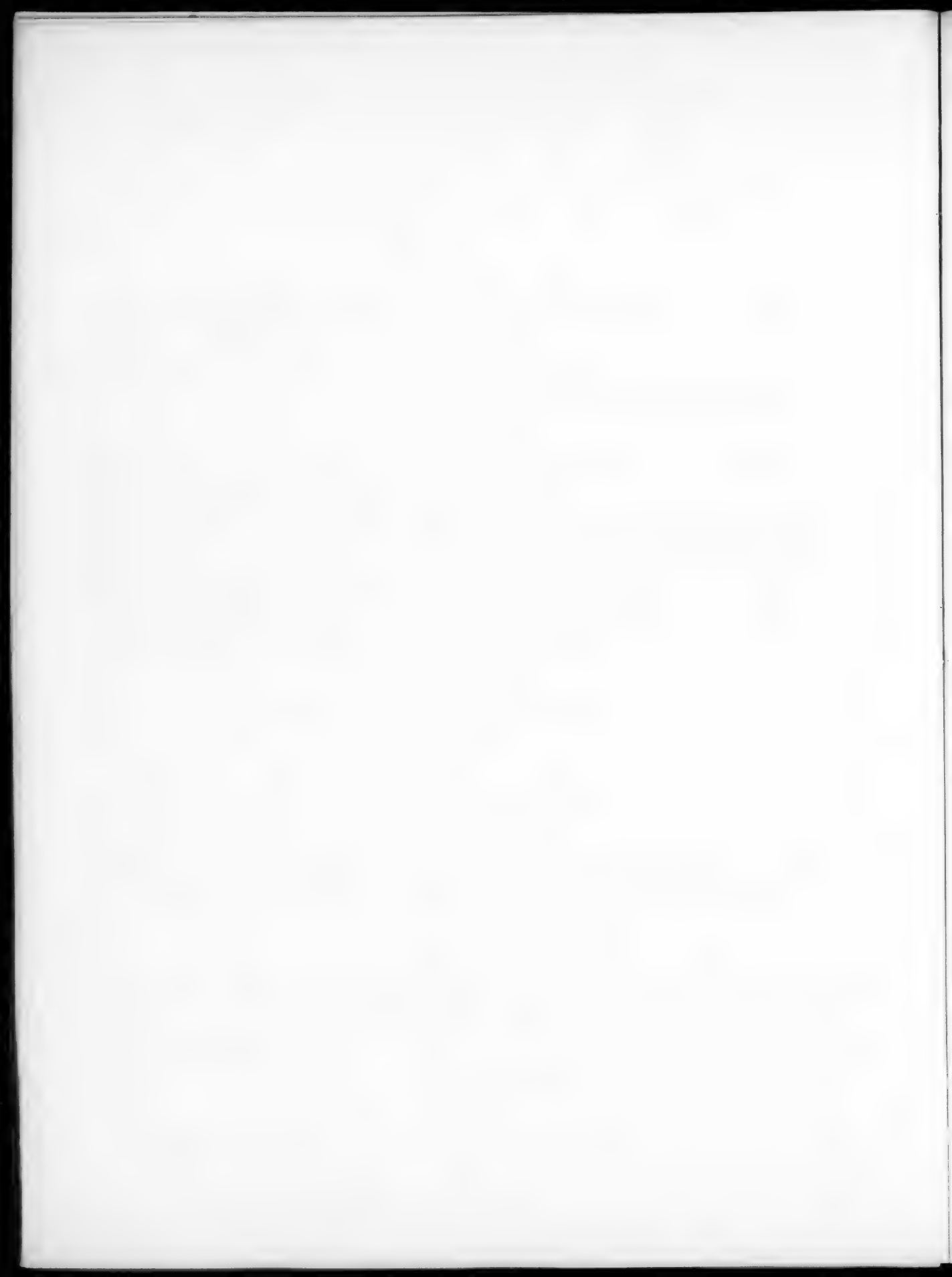


Fig. 2. Dependence of the solubility of sodium fluoride on the content of alcohol in the water-alcohol mixture at 25°.

changed. On the basis of the results obtained it is possible to come to the conclusion that for washing precipitates of binary and complex fluorides free from excess precipitant and other admixtures, water-alcohol



ON THE ROLE OF THE STATE OF THE SURFACE OF THE CATHODE IN THE

ELECTROREDUCTION OF AROMATIC NITRO COMPOUNDS

N. A. Izgaryshev and M. Ya Fioshin

The course of the electroreduction process of organic compounds depends to a large extent on the nature of the cathode material. One of the basic causes of the existence of this dependence is the hydrogen overvoltage. It is customary to assume that the greater the hydrogen overvoltage at the cathode, the higher its reducing properties, i.e., the more profoundly and intensively electroreduction process proceeds [1]. If the hydrogen overvoltage at the given cathode is small, then it is difficult to count on a high effectiveness of the reduction of organic depolarizers (in particular, if it belongs to the weak class), since at strong polarization the cathode begins to evolve hydrogen. Thus, during the reduction of nitrobenzene in acid medium on cathodes of zinc or lead the formation of aniline will proceed. By the use as cathode of platinum, the product of the incomplete reduction of nitrobenzene — phenylhydroxylamine [2] is formed. This is explained by the fact that at a platinum cathode the reduction potential of phenylhydroxylamine to aniline is more negative than the potential for the evolution of hydrogen; consequently in place of the reduction of phenylhydroxylamine the evolution of hydrogen will occur.

The direction and intensity of the process of electroreduction are determined not only by the nature of the cathode material.

Preliminary treatment of the cathode, consisting in placing on its surface a spongy (and in a number of cases dense galvanic) deposit of metals, pickling, mechanical treatment, etc. exerted a very substantial influence on the direction of the electroreduction process in a number of cases. Such preliminary treatment makes it possible to successfully reduce various organic compounds on metals with low hydrogen overvoltages. Tafel further noted the fact that on spongy lead the electroreduction proceeds with greater effectiveness than on smooth lead and proposed a method of special treatment of the surface of a lead cathode before the synthesis [3].

Lebedev and his coworkers, in the course of a study of the electrohydrogenation of vinylacetylene, established that the process proceeds with excellent yields only on copper or brass cathodes covered with platinum black [4]. On smooth platinum the process proceeds poorly. There are indications concerning the role of preparing the surface of the cathode in the electrohydrogenation of acetylenic alcohols in the works of Favorskaya [5] and Lebedeva [6].

The preliminary placing of various metals on the surface of the cathode by the galvanic method which considerably increases its reduction capacity has a substantial significance in a number of cases. Thus, in the reduction of methylethylketone Izgaryshev and Aryamova successfully used a copper cathode having the form of a spiral, covered with electrolytic lead [7].

Preliminary treatment of the cathode, which facilitates the increase in the effectiveness of the reduction of organic substances does not always lead to the simultaneous increase of hydrogen overvoltage on the cathode. On spongy metals, for example, the hydrogen overvoltage is lower than on smooth metals, while the effectiveness of the electroreduction in a number of cases is considerably greater. At the same time the lowering of the hydrogen overvoltage on the spongy cathodes sometimes reaches 0.4 V, in comparison with smooth cathodes [8]. There are cases in which on both cathodes on which the hydrogen overvoltage is great, the electroreduction proceeds with high effectiveness, while on other cathodes, also with great hydrogen overvoltage, the reduction process proceeds very poorly. This can be seen in the case of the electroreduction of 2-chloromethyl-4-nitrotoluene into o-4-xylidene, studied by Bereзовsky and Varkov [9]. These authors detected that the reduction of 2-chloromethyl-4-nitrotoluene proceeds with high yields on cathodes made of zinc and lead. The yield of o-4-xylidene is considerably lowered by the use as cathode of mercury or copper and is entirely unsatisfactory when the reduction is carried out on a cathode of tin.

Apparently, the fact of the absence of a known relation between the hydrogen overvoltage and the effectiveness of the cathode reduction, established for a large quantity of syntheses, argues in favor of the catalytic influence of the surface of the cathode on the electroreduction of a number of organic depolarizers. The fact that the surface of the metal can exert catalytic influence on the cathodic and anode processes is discussed in the work of Pecherskaya and Stender [10].

The object of our work was the study of the electroreduction process of o-, m- and p-nitrobenzoic acids into the corresponding aminobenzoic acids on various cathodes. It is necessary to make the reservation that we did not pursue the goal of establishing the dependence of the yields of aminobenzoic acids on the nature of the cathode. The present investigation should be considered as an attempt to find the relation between the state of the surface of each of the cathodes investigated and the yields of aminobenzoic acids at various temperatures, concentration of hydrochloric acid and current densities. A brief note on the work already carried out has been published previously by us [11].

EXPERIMENTAL

Apparatus and Method of Investigation. The reduction of nitrobenzoic acids was studied on cathodes of tin, lead, amalgamated zinc, copper and graphite. The cathodes consisted of perforated cylinders which were placed in a porous cylindrical diaphragm, which served as a cathode space. The anode was prepared from sheet lead. The nitrobenzoic acid was introduced into the cathode space in the form of a suspension in hydrochloric acid. 15% sulfuric acid served as the anolyte in all cases. The suspension of nitrobenzoic acid was stirred with a mechanical stirrer. To maintain the determined temperature the electrolyzer was placed in a thermostat supplied with a thermoregulator. The yields of aminobenzoic acids were determined by diazotization. The measurement of the melting points of the aminobenzoic acids evolved from the catholyte after completion of the electroreduction process proved to be in excellent agreement with the literature data.

The study of the influence of the state of the surface of the cathode on the yields of aminobenzoic acids was carried out at various temperatures, current densities, concentrations of hydrochloric acid and added quantities of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The reproducibility of the results of experiments carried out under identical conditions was excellent (1-2%).

1. **Study of the Influence of Temperature.** The nitrobenzoic acids in quantities of 5 g were reduced at various temperatures (20-75°) on cathodes of tin, lead, amalgamated zinc, copper and graphite. 2.32 N hydrochloric acid served as electrolyte, the current density at the cathode amounted to 8 A per square decimeter. In the reduction of the nitrobenzoic acids on cathodes of copper and graphite, good results could be obtained only in the presence of 1-7 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The introduction of this additive facilitated the increase in the yields of aminobenzoic acids according to substance, but lowered their yields according to current, since to eliminate the Cu^{++} ions from the solution an additional quantity of electricity was passed, which was taken into account in the calculation of the yield by current.

In Table 1 are set forth the yields of aminobenzoic acids by substance at various temperatures.

TABLE 1
Yields of Aminobenzoic Acids by Substance at Various Temperatures on Various Cathodes

Temp.	Yield of acids (in %)														
	o-Aminobenzoic					m-Aminobenzoic					p-Aminobenzoic				
	Sn	Pb	Zn + Hg	Cu	C	Sn	Pb	Zn + Hg	Cu	C	Sn	Pb	Zn + Hg	Cu	C
20°	65.7	48.8	68.0	68.7	—	91.6	60.1	72.3	72.8	42.6	29.3	5.4	—	—	—
30	94.5	81.4	87.8	73.2	38.4	96.7	69.4	90.1	75.4	52.2	38.9	13.0	—	11.4	18.2
40	98.0	88.2	96.5	65.2	42.6	95.6	85.1	90.9	73.2	83.3	51.6	34.2	—	28.5	43.7
50	99.0	86.9	97.3	52.6	42.9	97.0	84.8	95.0	—	74.5	63.4	67.1	—	46.4	76.8
60	98.5	85.4	97.5	48.7	—	97.2	85.8	94.8	84.3	62.4	93.4	87.9	—	69.1	66.9
70	97.7	84.2	97.3	—	—	92.2	77.8	95.1	82.7	50.4	94.6	88.1	—	78.4	70.4
75	96.8	—	97.8	—	—	90.1	—	94.7	80.6	—	95.3	84.7	—	73.8	70.9

Observations on the course of the syntheses showed that in the first instants after switching on the current a precipitate of copper is formed on cathodes of copper and graphite. This was particularly noticeable on graphite. The source of the copper which settled out on the copper and graphite cathodes was the Cu^{++} ions introduced into the catholyte in the form of the chlorous salt. With the use as cathode material of tin a considerable portion of the nitrobenzoic acids was reduced chemically, apparently, due to the reaction $\text{Sn}^{++} \rightarrow \text{Sn}^{+++}$.

It was indicated in one of the works that the yields of p-aminobenzoic acid on cathodes of tin and lead reached 98% only in the presence of 3-5 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ per 5 g p-nitrobenzoic acid [12]. We showed that it is in general possible to avoid the use of stannous chloride but at the same time is necessary to increase the intensity of stirring the suspension of p-nitrobenzoic acid by 3-4 times.

Apparently in the work of the above mentioned authors the intensity of stirring was insufficient for regular

intake of p-nitrobenzoic acid at the cathode and its electrochemical reduction. The role of the introduced addition of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ probably consisted in the chemical reduction of that portion of the p-nitrobenzoic acid which, due to the insufficient effectiveness of the stirring, did not succeed in reaching the cathode. It is noteworthy that in all cases in which the cathode is formed of light sponge with a developed surface, the yields of aminobenzoic acids are increased, and, on the contrary, the formation of a dark precipitate on the surface of copper or graphite cathodes facilitates a marked reduction in the yields. The behavior of the lead cathode is very interesting. The study of the results of the synthesis on a lead cathode shows a considerable dependence of the yields of aminobenzoic acids on the temperature. This is probably associated with increased solubility of lead in hydrochloric acid with increased temperature. Since the unique source of the lead ions by the discharge of which the formation of sponge on the cathode proceeds, is the material of the cathode, it is understandable that at higher temperatures the sponge will have a maximal surface. The increase in the effectiveness of the reduction in this case cannot be ascribed to anything other than the spongy structure of the surface of the cathode. The $^{++}$ participation of the Pb^{++} ions in the reduction reaction is excluded, since divalent lead does not have reducing properties. Attempts to reduce p-nitrobenzoic acid at a cathode of amalgamated zinc did not give positive results. This is explained by the fact that p-nitrobenzoic acid is poorly suspended in hydrochloric acid, while since upon dissociation of the amalgam there proceeds strong evolution of hydrogen, a foam is formed which is discharged from the electrolyzer and carries away particles of p-nitrobenzoic acid. The great losses of p-nitrobenzoic acid under these conditions distort the results and compelled us to withhold this isomer from reduction at a cathode of amalgamated zinc.

2. Study of the Influence of Additives. Additions of the salts of metals which facilitate the increased effectiveness of the electroreduction of organic substances, can be separated into 2 groups.

No particular doubts arise relative to the mechanism of action of polyvalent ions of the metals. Ions of the Ti^{+++} , Fe^{++} , Cr^{++} , V^{++++} type and others, introduced into the catholyte in the form of salts in which they have a lower valence, chemically reduce the organic substances and are thereby converted into the higher valence. At the cathode reduction of the ions of higher valence into ions of lower valence proceeds, which latter react anew with the organic substance etc. Such ions are sometimes called "hydrogen carriers" [13].

The salts of metals which belong to the other group (salts of zinc, mercury, lead and others) have another mechanism of action which consisted in precipitation at the cathode and increasing the hydrogen overvoltage, since it is well known that on zinc, mercury and lead the hydrogen overvoltage is great. The addition to the catholyte of salts of zinc, mercury, lead, can, for example, permit the reduction of nitrobenzene into aniline with excellent yields even at cathodes with low overvoltages where, in the absence of catalytic additives, the evolution of hydrogen [14] will chiefly proceed.

However, the question of the mechanism of action of these catalytic additives has still not been entirely clarified. For example, it is well known that upon the introduction into the catholyte of copper salts or powdered copper a marked increase in the effectiveness of the reduction of aromatic nitrocompounds occurs. This is explained by the fact that copper and also zinc or tin can be precipitated on the cathode and chemically reduce the nitrocompound to amine. Since in the reduction of aromatic nitrocompounds the most difficult stage which determines the rate of the entire process as a whole, is the conversion of the phenylhydroxylamine into the corresponding amine, it is assumed that zinc, tin or copper, precipitated at the cathode, specifically reduce phenylhydroxylamine, thereby increasing the rate of the process as a whole. The absence of complete clarity in the question of the influence of added salt on the process of electroreduction impelled us to study this question in the case of the nitrobenzoic acids. Particular attention was paid to the establishing of a relation between the yields of aminobenzoic acids by substance and the character of the deposits of metallic copper on the cathode. The cathodes were prepared from copper and graphite. The results of the experiments are presented in Table 2.

TABLE 2

Influence of Additions of Cuprous Chloride on the Yields of Aminobenzoic Acids by Substance on Copper and Graphite Cathodes

Concentration of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (in g)	Yield of acids (in %)					
	o-Aminobenzoic		m-Aminobenzoic		p-Aminobenzoic	
	Cu (30°)	C (40°)	Cu (60°)	C (40°)	Cu (70°)	C (60°)
0	65.3	42.6	63.5	69.9	56.3	67.2
1	73.2	72.8	84.3	83.3	78.4	76.1
3	85.9	73.9	78.0	79.4	80.5	81.5
5	83.2	78.3	79.7	79.1	80.3	79.8
7	—	77.6	78.5	78.7	78.2	84.7

As has already been indicated, the introduction of additions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ lowers the yield by current, since it increases the quantity of electricity consumed for the evolution of copper from the solution; consequently the introduction of additions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is expedient only in those cases when the effect in increasing the yields by substance justifies the additional consumption of electric energy. It is evident from Table 2 that in the majority of cases there exists some limit on the quantity of cuprous chloride introduced into the catholyte, above which no further increase in the yields of aminobenzoic acids by substance occurs. This is apparently explained by the fact that the duration of the electrolysis increases due to the time which is necessary to precipitate the copper from the solution. The increase in the duration of the electrolysis is associated with the emergence of undesirable side processes, in which intermediate and final products of the reduction of nitrobenzoic acids participate and which is associated with the observed reduction in the yields by substance on increase in the quantity of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ introduced into the catholyte.

3. Study of the Influence of the Concentration of Hydrochloric Acid. The data which characterize the yields of aminobenzoic acids at various concentrations of hydrochloric acid, are presented in Table 3.

In the majority of cases the change in the concentration of HCl is not appreciably reflected in the yields of aminobenzoic acids. Only o-nitrobenzoic acid appears to be an exception; during its reduction on a graphite cathode a fall in the yields of o-aminobenzoic acids with increase of HCl concentration is observed; at the same time a considerable quantity of side products appears in the catholyte. Evidently, this is 5-hydroxyanthranilic acid [15].

4. Study of the Influence of Current Density at the Cathode. The current density, as is well known, is an important factor on which very often depends the direction of the electroreduction process, and consequently, the nature of the end product.

The data of the influence of current density on the yields of aminobenzoic acids are presented in Table 4.

As is evident from the data of Table 4, the yields of aminobenzoic acids only slightly depend on the current density when tin and amalgamated zinc are used as the cathodes. This indicates the great rate of reduction of nitrobenzoic acids at a tin cathode, apparently due to the reaction $\text{Sn}^{++} \rightarrow \text{Sn}^{+++}$, i.e., due to chemical reduction,

TABLE 3
Yields of Aminobenzoic Acids by Substance at Various Concentrations of HCl on Various Cathodes

Concentration of HCl (N)	o-Aminobenzoic Acid					m-Aminobenzoic Acid					p-Aminobenzoic Acid			
	Sn (50°)	Pb (40°)	Zn + Hg (50°)	Cu (30°)	C (40°)	Sn (60°)	Pb (60°)	Zn + Hg (50°)	Cu (60°)	C (40°)	Sn (70°)	Pb (70°)	Cu (60°)	C (70°)
0.58	98.3	76.1	92.5	87.4	87.5	95.7	83.9	91.4	65.6	81.9	94.0	81.4	74.6	82.0
1.16	98.8	79.2	94.4	90.7	82.3	96.5	84.9	92.3	63.2	81.8	94.1	86.1	76.3	82.8
1.74	97.7	86.5	97.9	89.9	78.6	96.1	85.1	95.0	69.2	82.3	94.1	84.5	78.6	83.0
2.32	99.0	88.2	97.4	85.9	78.3	97.2	85.8	95.0	84.3	83.3	94.6	87.9	80.5	84.7
2.9	97.9	85.2	97.7	86.6	71.3	97.0	85.3	95.1	84.0	82.7	94.7	87.5	82.4	85.4
3.48	96.1	84.1	98.0	85.8	70.0	97.1	82.4	94.3	91.4	82.4	94.9	90.7	81.4	85.3
4.06	95.4	82.8	96.7	85.7	—	95.2	82.2	95.4	94.4	82.7	95.3	93.7	82.4	80.3

TABLE 4
Yields of Aminobenzoic Acids by Substance at Various Current Densities on Various Cathodes*

Current density at the cathode A/ dm ²	Yield of acids (in %)													
	o-Aminobenzoic					m-Aminobenzoic					p-Aminobenzoic			
	Content of HCl (N)													
	2.32	2.32	2.32	1.16	0.58	2.32	2.32	2.32	4.06	2.36	2.32	4.06	2.9	3.48
	Sn	Pb	Zn + Hg	Cu	C	Sn	Pb	Zn + Hg	Cu	C	Sn	Pb	Cu	C
2	95.4	70.8	95.9	72.5	58.1	90.6	70.6	93.2	94.3	66.2	93.4	83.0	79.0	—
4	96.8	87.4	98.6	90.4	75.8	94.2	72.3	93.9	94.3	72.9	94.8	87.1	72.6	81.1
6	98.5	86.3	98.1	91.2	84.8	95.3	74.2	93.6	97.7	81.5	94.2	93.4	73.6	87.2
8	99.0	88.2	97.3	90.7	87.5	97.2	85.8	95.0	94.4	83.3	94.6	93.7	82.4	85.3
10	98.3	84.1	97.2	86.3	86.6	95.6	83.1	95.4	93.5	83.3	94.7	94.3	81.6	81.9
12	95.5	83.4	97.5	87.6	90.8	90.9	82.4	95.4	93.9	81.8	98.0	95.0	82.2	82.1
14	92.3	79.8	97.3	72.9	92.0	84.4	81.9	93.9	87.2	79.2	96.0	93.2	80.3	—

* The experiments were carried out at the same temperatures as in Table 3.

As regards a cathode of amalgamated zinc, reduction on it probably proceeds not as a result of the passage of a

polarizing current, but basically due to decomposition of the amalgam. Electrons, freed by the decomposition of the zinc amalgam, enter into the reduction of the organic substance. A portion of the electrons is consumed by the evolution of hydrogen, which was also observed by us at the time of synthesis. Very interesting results were obtained at the lead cathode. In an already mentioned work [12] the authors reduced p-nitrobenzoic acid at a lead cathode and obtained a maximal yield at a current density of 6 A per square decimeter in the presence of 5 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$.

Increasing the number of rotations of the stirrer by approximately 3 times, we obtained such yields as in the mentioned work, but at a current density of 12 A per square decimeter and in the absence of any additive. In the majority of cases diminishing the current density to 2 A per square decimeter caused a drop in the yield of aminobenzoic acids due to increase in the electrolysis time and consequently, creation of favorable conditions for the development of side processes. An interesting fact which confirms the existence of a profound relation between the state of the cathode surface and the electroreduction process was noted during the reduction of p-nitrobenzoic acid at a copper cathode. At current densities of 4-6 A per square decimeter in the presence of 3 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ a dark precipitate is formed on the copper cathode which is accompanied by lowering of the yield of p-aminobenzoic acid. By reducing the current density to 2 A per square decimeter in place of the expected further lowering of the yield an increase in it was observed, in spite of the fact that the electrolysis time was increased in comparison with the preceding experiment (at 4 A per square decimeter) by 2 times. The increased yield of p-aminobenzoic acid at 2 A per square decimeter, apparently, is facilitated by the dense, bright covering of copper, which is formed on the cathode. The "black" which is formed at the surface of the copper cathode at 4-6 A per square decimeter, probably lowers its activity to some extent.

DISCUSSION OF RESULTS

The results of the study of the process of electroreduction of nitrobenzoic acids under various conditions makes it possible to establish the existence of a relationship between the yields of aminobenzoic acids and the state of the cathode surface. On cathodes of graphite and copper in the absence of additions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ we did not succeed in obtaining good yields of aminobenzoic acids. The most probable cause of this is the insufficiently high hydrogen over-voltage on copper and graphite. Copper ions, introduced into the catholyte, are destroyed at the cathode with the formation of a metallic precipitate. The effectiveness of the reduction depends on the form of the precipitate. The highest yields of aminobenzoic acids were achieved when a bright sponge having a developed surface, is formed on the cathode. The sponge on the surface of the cathode unmistakably shows catalytic action on the process of electroreduction. The mechanism of action of the sponge can, in our opinion, be represented in the following manner:

1. The finely dispersed sponge can chemically reduce the nitrobenzoic acids to aminobenzoic acids. Lukashevich showed that copper in a finely disperse state is capable of reducing nitrobenzene to aniline [16].

However the role of sponge in the electrochemical synthesis of organic compounds is not exhausted by participation in the process only as a chemical reductant. Lukashevich in the same work reported that finely disperse lead does not have high reducing properties and is capable of reducing nitrobenzene only to phenylhydroxylamine. The rate of the reduction of the latter to aniline is very small. The property of finely disperse lead, established by Lukashevich, clearly does not correspond with the results obtained by us in the electroreduction of nitrobenzoic acids on a spongy lead cathode. In those cases when a lead sponge appears on the cathode, the effectiveness of the reduction is increased and to a greater extent, the greater the volume of the sponge formed. Taking into account the fact that the hydrogen overvoltage on the sponge is less than on a smooth cathode, its role in the processes of electrochemical reduction of organic substances may be determined otherwise than in the first case.

2. In organic syntheses copper in the finely disperse state is widely used as a catalyst [17]. The role of the catalyst consists in lowering the activation energy of the reaction due to adsorption of molecules of the organic substance on the surface of this catalyst. The greater the surface of the catalyst, the higher its capacity for adsorption. During the adsorption there takes place deformation of the molecules of the organic substance which proceeds under the action of the force field of the catalyst surface. The deformation leads to disruption of the bonds in the molecule and to increase in its reactivity [18]. It was established that copper and lead catalyze the reaction of chemical reduction of nitrobenzene into aniline in which the reducing agent is hydrogen. The use of finely disperse lead makes it possible to obtain aniline in a yield equal to 97% [19].

The spongy surface of the cathode responds as well as possible to the demands presented to the active catalysts. On a spongy cathode surface adsorption of molecules of nitrobenzoic acids proceeds and leads to their deformation which is manifested in increase in the dipole moment constant. In a comparison of the dipole moments of many organic substances with the reduction potentials of these substances Voitkevich detected that with increase in the dipole moment the reduction potential becomes more positive, i.e., the depolarizing action of the substance is increased [20]. Thus, increase in the dipole moment which proceeds as a result of the adsorption of nitrobenzoic acid molecules apparently appears to be one of the basic causes of the increase in the effectiveness of reduction on a spongy cathode.

[17]. N. N. Vorozhtsov. Fundamentals of the Synthesis of Intermediate Products and Dyes. Moscow - Leningrad, 828 (1950).

[18]. B. N. Dolgov, Catalysis in Organic Chemistry. Moscow - Leningrad, 94 (1949).

[19]. F. A. Madenwald, C. O. Henke, O. W. Brown, Chem. Zentr., II, 779 (1927).

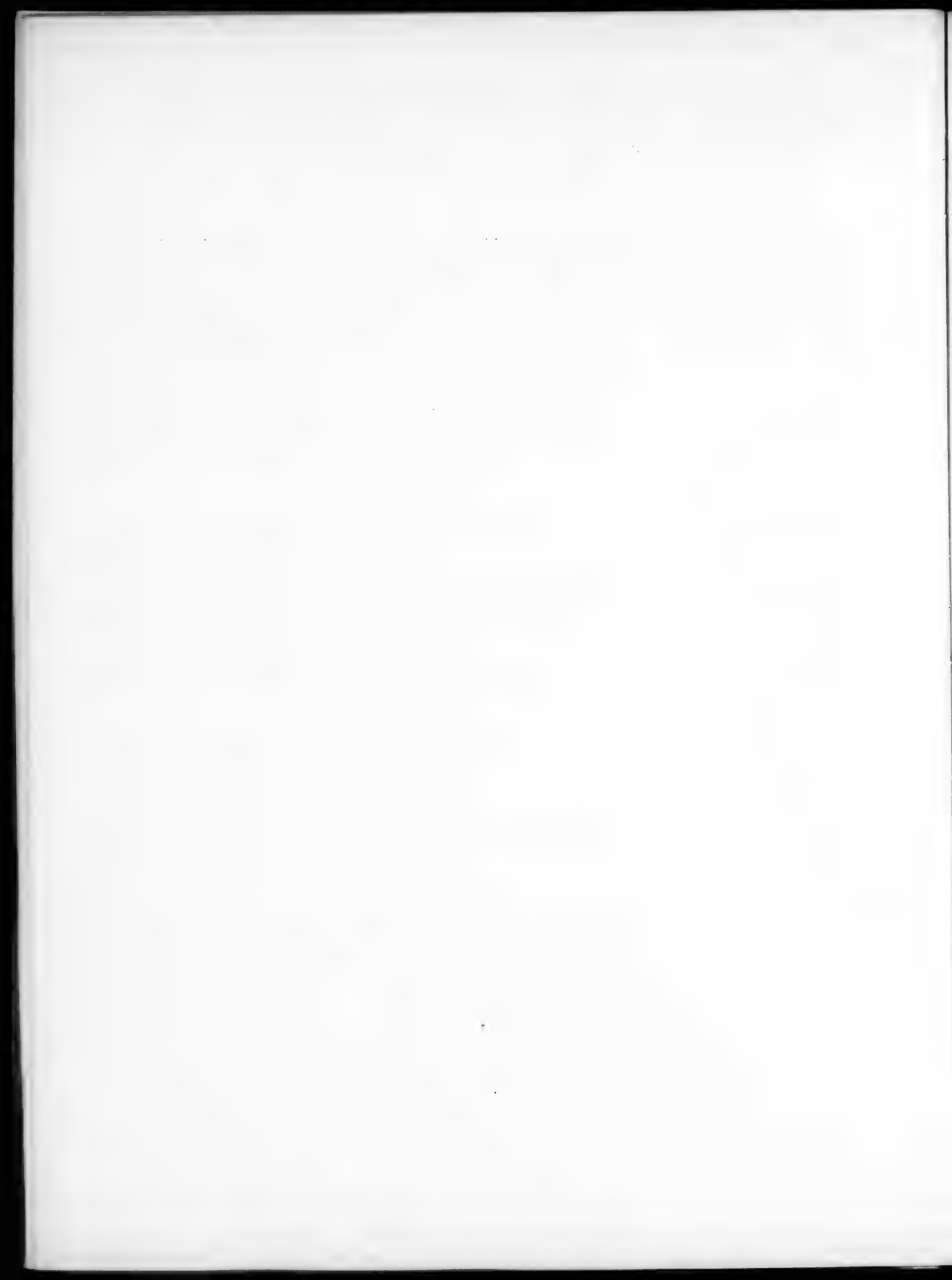
[20]. S. A. Voitkevich, J. Phys. Chem., 26, 869 (1952).

[21]. L. I. Antropov. Transactions of the Second All-Union Conference on Theoretical and Applied Electrochemistry (1949); J. Phys. Chem., 24, 1428 (1950); 25, 1494 (1951).

[22]. N. A. Izgaryshev and M. Ya. Fioshin, Proc. Acad. Sci. USSR, 90, 581 (1953).

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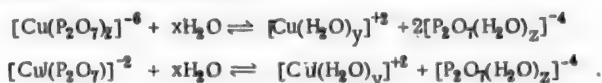
ON THE COMPOSITION AND PROPERTIES OF THE COMPLEX ELECTROLYTE OF THE COPPER-PYROPHOSPHATE BATH

E. A. Ukshe and A. I. Levin

The solution of the problem of the mechanism of electrode processes during the electroprecipitation of metals from solutions of their complex salts can not be accomplished without detailed study of the composition and properties of the complex ions which are found in the electrolyte. This situation is of a general character and, consequently in studying the possibility of the galvanic precipitation of copper from pyrophosphate bath we encountered the necessity of specially considering the question of its composition.

It is necessary to note that in the last few years a number of investigations of the composition and stability of complex ions of copper pyrophosphate have appeared. The analysis of the available data permits the following conclusions to be made.

Depending on the pH and concentration of the components, when solutions of copper sulfate and sodium pyrophosphate were mixed the following ions were detected: $[\text{Cu}(\text{P}_2\text{O}_7)]^{-2}$; $[\text{Cu}(\text{P}_2\text{O}_7)_2]^{-6}$; $[\text{Cu}(\text{HP}_2\text{O}_7)(\text{P}_2\text{O}_7)]^{-5}$; $[\text{Cu}(\text{HP}_2\text{O}_7)_2]^{-4}$; $[\text{Cu}(\text{P}_2\text{O}_7)(\text{OH})]^{-3}$. The first two complexes appeared as a result of the general complex formation reaction and naturally participate in solvation equilibria of the type [1]:



The instability constant of the $[\text{Cu}(\text{P}_2\text{O}_7)_2]^{-6}$ ion has been determined by many investigators: Stabrovsky [2] cited the value $K_{\text{inst.}} = 3.1 \cdot 10^{-10}$, Rogers and Reynolds [3] $K_{\text{inst.}} = 2 \cdot 10^{-11}$ and, finally Waters and Aaron [4] $K_{\text{inst.}} = 2 \cdot 10^{-9}$. There are many contradictory data for the instability constants of the $[\text{Cu}(\text{P}_2\text{O}_7)]^{-2}$ ion.

As is well known from the literature data, both complexes under consideration can exist in the pH range approximately from 7 to 10 [4]. In addition, there is an indication [4] of the existence of the complexes $[\text{Cu}_2\text{P}_2\text{O}_7]^0$ and $[\text{Cu}_4(\text{P}_2\text{O}_7)]^{+4}$, but these ions, apparently, are only formed in very dilute solutions.

In a number of cases the solvation equilibria in copper-pyrophosphate solutions can be complicated by side reactions of the acid-base type.

Thus, at pH > 10 the following equilibrium takes place:



Similar complex cuprate-pyrophosphate anion was detected by a number of authors [5,6] and its instability constant was equal, according to their data, to $6 \cdot 10^{-14}$ or $2 \cdot 10^{-16}$.

At pH > 11 the copper-pyrophosphate complex is destroyed and a precipitate of cupric oxide hydrate settles out.

In acidic solutions equilibria are possible which lead to the formation of complex copper-pyrophosphate ions containing the $(\text{HP}_2\text{O}_7)^{-3}$ group. At pH 5.3-7.0 the formation of the ion $[\text{Cu}(\text{HP}_2\text{O}_7)(\text{P}_2\text{O}_7)]^{-5}$ with an instability constant of 10^{-10} [6] was noted, while at pH < 5.3 the ion $[\text{Cu}(\text{HP}_2\text{O}_7)_2]^{-4}$ with an instability constant close to $4 \cdot 10^{-9}$ [6] was noted. The study of the latter complexes was complicated in connection with the fact that in acid solutions a precipitate of the hypothetical composition $\text{Na}_2\text{Cu}_3(\text{P}_2\text{O}_7)_2$ settled out [6].

As is evident from the information set forth on the stability of copper pyrophosphate complexes, there is one very substantial hiatus in them—this is the sharp discrepancy of the available data on the instability constant of the $[\text{Cu}(\text{P}_2\text{O}_7)]^{-2}$ complex. At the same time, the precise knowledge of this quantity is necessary to elucidate the concrete picture of the composition of the copper-pyrophosphate solutions of varying concentration. Its knowledge is also important for the solution of the question of the mechanism of electrode reactions in a copper-pyrophosphate bath.

To fill this gap we calculated the instability constants of the complex ions $[\text{Cu}(\text{P}_2\text{O}_7)_2]^{-6}$ and $[\text{Cu}(\text{P}_2\text{O}_7)]^{-2}$ on the basis of analysis of the data on the measurement of the potentials of a copper electrode in the corresponding solutions.

The potentials were measured by the usual compensation method with the methodology not differing from that generally adopted [7].

The results of the indicated measurements are set forth in Table 1.

In the calculations of the instability constant we start from the equations:

$$K_1 = \frac{[P_2O_7^{4-}][Cu^{+2}]}{[Cu(P_2O_7)^{-2}]} \quad \text{and} \quad K_2 = \frac{[P_2O_7^{4-}]^2[Cu^{+2}]}{[Cu(P_2O_7)_2^{-6}]}$$

When the excess of $P_2O_7^{4-}$ ions is so great that one can assume the formation almost exclusively of $[Cu(P_2O_7)_2]^{-6}$ ions, the concentration of these ions is practically equal to the initial concentration of copper (C_{Cu}^0), while $[P_2O_7^{4-}]$ is respectively equal to the initial concentration of pyrophosphate after deducting $2C_{Cu}^0$. Thus $[Cu^{+2}] = \frac{K_2 C_{Cu}^0}{C_{P_2O_7}^0 - 2C_{Cu}^0}$

and therefore

$$E - E_{Cu}^0 = 0.03 \log \frac{K_2 C_{Cu}^0}{C_{P_2O_7}^0 - 2C_{Cu}^0} = 0.03 [\log K_2 + \log C_{Cu}^0 - \log (C_{P_2O_7}^0 - 2C_{Cu}^0)] \quad (1)$$

Evidently, when the initial concentration of pyrophosphate is close to the initial concentration of copper, the formation of the complex $[Cu(P_2O_7)_2]^{-6}$ is difficult to expect and then

$$E - E_{Cu}^0 = 0.03 [\log K_1 + \log C_{Cu}^0 - \log (C_{P_2O_7}^0 - C_{Cu}^0)] \quad (2)$$

It should be noted that the available literature data for K_1 are either such that K_1 is approximately equal to K_2 , or they correspond to the inequality $K_2 \ll K_1$. In the first case the conditions for fulfilling equation (1) are in general difficultly attainable. On the other hand, the conditions for fulfilling equation (2) can be obtained comparatively readily. They correspond to the first 5 systems set forth in Table 1.

TABLE 1

Potentials of a Copper Electrode in the System $CuSO_4 - Na_4P_2O_7 - H_2O$ and the Instability Constants of the Copper-Pyrophosphate Complexes at 25 °C

System no.	Concentration (in moles)		Assumed predominant form	E (in volts)	log $K_{inst.}$
	$CuSO_4$	$Na_4P_2O_7$			
1	0.0050	0.0050	$[Cu(P_2O_7)]^{-2}$	+0.198	-7.4
2	0.0100	0.0100		+0.219	-6.3
3	0.0200	0.0200		+0.222	-6.3
4	0.0200	0.0300		+0.172	-6.0
5	0.0300	0.0500		+0.162	-6.2
6	0.0050	0.0300	$[Cu(P_2O_7)_2]^{-6}$	+0.035	-9.8
7	0.0200	0.1000		+0.011	-10.6
8	0.040	0.100		+0.052	-10.2
9	0.040	0.200		-0.010	-10.5
10	0.20	0.500		+0.004	-11.5

The data of Waters and Aaron prove to correspond more with the actual conditions and therefore equation (1) can also be used in the determined limits.

Thus the obtained value for K_1 is $0.63 \cdot 10^{-6}$ and for K_2 is $0.5 \cdot 10^{-10}$. The values found for K_2 are found in agreement with the data of other authors [2,3] and the ratio of the constants satisfies the Babko-Khodakov condition [9]:

$$\frac{\log K_2 - \log K_1}{\log K_1} = \frac{P_2 - P_1}{-P_1} \quad (3)$$

where P_1 and P_2 are the energetic characteristics of the complexes, equal to -8 and -14 respectively [10].

Actually, if K_1 is approximately equal to 10^{-8} , then according to equation (3)

$$\log K_2 = \frac{14 + 8}{8} (-6) = -1.75 \cdot 6 = -10.50.$$

On the basis of the obtained values of the instability constants a graph of the dependence of the contents of various complex forms in solution on the concentration of free pyrophosphate can be constructed.

The calculation was carried out according to the equations:

$$[Cu^{+2}] = \frac{100\%}{1 + \frac{[P_2O_7^{4-}]}{K_1} + \frac{[P_2O_7^{4-}]^2}{K_2}} \quad (4)$$

$$[Cu(P_2O_7)^{-2}] = [Cu^{+2}] \frac{[P_2O_7^{4-}]}{K_1}; \quad [Cu(P_2O_7)_2^{-6}] = [Cu^{+2}] \frac{[P_2O_7^{4-}]^2}{K_2}$$

The results of the calculation are presented in Fig. 1; it follows from its data that the concentration of the $[Cu(P_2O_7)]^{-2}$ anion is maximal only in a narrow interval of values for the concentration of $[P_2O_7^{4-}]$, and this form in the best case contains only 50% in all of copper and generally can not predominate; it is therefore clear that the calculated value of the instability constant K_1 is somewhat low, but this has no further theoretical significance and it can be confirmed that the ratio $\log K_2 : \log K_1$ is close to 2 in each case.

Such a conclusion is in complete agreement with the data of Waters and Aaron [4]. Its verification can be accomplished by means of the determination of the conductance of the system $CuSO_4 - Na_4P_2O_7 - H_2O$. The measurements were carried out by the usual method with the aid of a variable current bridge.

The temperature was held at $20 \pm 0.2^\circ$. The results of the measurements are presented in Table 2 and in Fig. 2 and bear witness to the existence of points of inflexion on the curves $\kappa = f(C)$, corresponding to the condition $[Na_4P_2O_7] : [CuSO_4] = 3 : 2$.

TABLE 2

Conductance of the System $CuSO_4 - Na_4P_2O_7 - H_2O$ at 20°

Concentration (in moles)		κ , ohms $^{-1}$ cm $^{-1}$	Concentration (in moles)		κ , ohms $^{-1}$ cm $^{-1}$
$CuSO_4$	$Na_4P_2O_7$		$CuSO_4$	$Na_4P_2O_7$	
0.020	0.020	0.0045	0.020	0.080	0.0134
0.020	0.025	0.0058	0.020	0.090	0.0242
0.020	0.030	0.0069	0.030	0.060	0.0094
0.020	0.035	0.0072	0.040	0.060	0.0083
0.020	0.040	0.0078	0.040	0.080	0.0123
0.020	0.045	0.0085	0.040	0.100	0.0160
0.020	0.050	0.0091	0.040	0.200	0.0240
0.020	0.060	0.0104	0.050	0.060	0.0111
0.020	0.070	0.0118	0.050	0.100	0.0153

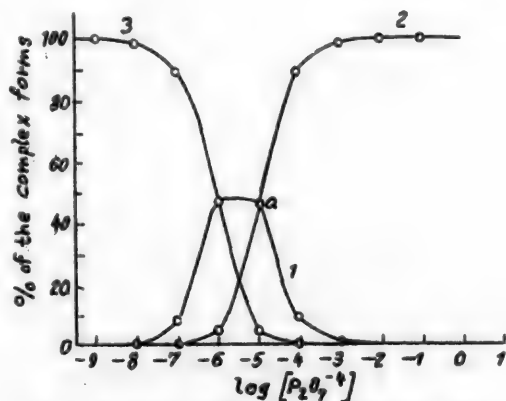


Fig. 1. Relative concentrations of the complex forms in the system $Cu^{+2} - P_2O_7^{4-}$

1) $[Cu(H_2O)_6]^{+2}$, 2) $[Cu(P_2O_7)]^{-2}$, 3) $[Cu(P_2O_7)_2]^{-6}$

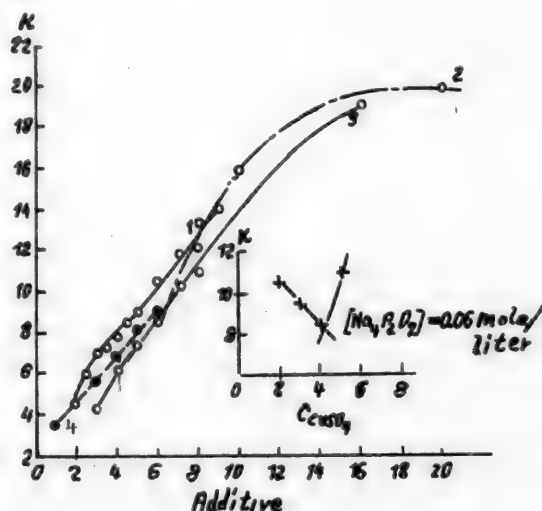


Fig. 2. Influence of complex formation on the conductance.

1) 0.02 m. $CuSO_4 + Na_4P_2O_7$, 2) 0.04 m. $CuSO_4 + Na_4P_2O_7$, 3) 0.01 m. $CuSO_4 + Na_2C_2O_4$, 4) 0.02 m. $CuSO_4 + Na_2C_2O_4$

As can be concluded without difficulty, this point closely coincides with the point *a* on Fig. 1 and almost completely coincides with the transfer of copper into the $[Cu(P_2O_7)_2]^{-6}$ ion. The presence of such an inflexion is readily

explained by the data obtained for the instability constant of the complex ions of copper pyrophosphate.

Thus, the results of the investigation show that under ordinary conditions the predominant ion in copper-pyrophosphate complex electrolyte is the $[\text{Cu}(\text{P}_2\text{O}_7)_2]^{-6}$ ion. Inasmuch as the working conditions for a pyrophosphate bath are characterized by the following data: pH 7.5–9.0, $[\text{Na}_4\text{P}_2\text{O}_7] : [\text{CuSO}_4] \geq 2$, this ion is practically uniquely capable of participating in the cathode process since the concentration of all other forms of the complex compounds is extraordinarily small.

Another important conclusion from the data obtained consists in the fact that with further refinements in the pyrophosphate bath a ratio of concentrations $[\text{Na}_4\text{P}_2\text{O}_7] : [\text{CuSO}_4] \leq 2$, should be obtained, since under these conditions the nature of the stimulating ions is scarcely changed while the lowering of the concentration of free pyrophosphate presents a greater perspective, inasmuch as in this case the crystallization of the $\text{Na}_4\text{P}_2\text{O}_7$ salt at the surface of the cathode becomes scarcely probable [8]. The ensuring of a sufficiently satisfactory solubility of the anodes during the electrolysis can be achieved by addition to the electrolyte of sodium citrate and other side substances which form quite soluble but not very stable complexes with copper. A similar ratio of concentrations of CuSO_4 and $\text{Na}_4\text{P}_2\text{O}_7$ with simultaneous introduction of substances which form collateral complexes in practice was accomplished by us and led to completely satisfactory results.

SUMMARY

1. The question of the composition of complex ions in a real pyrophosphate electrolyte, suitable for galvanic copper plating was considered.
2. The instability constants of complexes of copper pyrophosphate were measured potentiometrically. The values found for K_1 were $0.63 \cdot 10^{-6}$, and for K_2 , $0.5 \cdot 10^{-10}$.
3. The dependence of the conductance of the system



on the concentration of the components was studied. An inflexion point on the conductance curves, which corresponded to practically complete transfer of copper into the complex ion, was detected.

LITERATURE CITED

- [1]. A. A. Grinberg. Chemistry of Complex Compounds. Moscow – Leningrad (1952).
- [2]. A. I. Stabrovsky, J. Phys. Chem., 26, 949 (1952).
- [3]. Rogers, Reynolds, J. Am. Chem. Soc., 71, 2081 (1949).
- [4]. Waters, Aaron, J. Am. Chem. Soc., 75, 611 (1953).
- [5]. Eriksson, Kgl. Lantbruks Högskol Annalen (C. A., 1950, 3392), 16, 39 (1949).
- [6]. Onstott, Laitinen, J. Am. Chem. Soc., 72, 4724 (1950).
- [7]. A. I. Levin, E. A. Ukshe, V. S. Kolevatova, Proc. Acad. Sci. USSR, 88, 97 (1952).
- [8]. A. I. Levin, E. A. Ukshe, Proc. Acad. Sci. USSR, 91, 119 (1953).
- [9]. A. K. Babko, J. Gen. Chem., 15, 745 (1945).
- [10]. Yu. V. Khodakov. Elements of Electrostatic Chemistry. Moscow. (1934).

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INVESTIGATION OF THE STRUCTURAL CHANGES IN IRON-NICKEL-ALUMINUM ALLOYS BY THE TRUE HEAT CAPACITY METHOD

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In spite of numerous investigations [1,2] up to the present time there has been no consensus of opinion on the origin in iron-nickel-aluminum alloys of a high coercivity. Some [3] consider that the anomalously high coercivity (H_c) is caused by ordering processes of the high temperature phase β' , others [4,5,6] by its dispersion decomposition into the phases β and β' . Tretyi [7] assumes that in the dispersed solid the austenite α -phase also participates. A number of other questions, which are undoubtedly of practical importance, also remain unexplained. On the composition diagram of the system Fe-Ni-Al the boundaries of the concentration region of existence of the high coercivity alloys are not specified, the thermodynamic properties of the phases of this region are not clear, and the structural changes involved in achieving the high coercivity alloys are not established.

The present work is devoted to the study of the structural changes in Fe-Ni-Al alloys in the process of their magnetic hardening (increased coercivity), and to the establishment of the relation of these changes to the changes in magnetic properties. The investigation was carried out by the true heat capacity method.

As is well known, the method of true heat capacity is one of the most sensitive methods of investigating the changes in the physical state of a solid body. With its aid, a considerable variety of the forms of conversion which take place in solid phases has been detected. In a whole series of metallic systems the presence of so called conversions of the second type which include the changes associated with the processes of ordering, ageing, appearance and disappearance of magnetic properties, etc. was shown.

The method of true heat capacity also permits the quantitative evaluation of the conversion heat effects which proceed in solid alloys and makes it possible to judge concerning the rates of these conversions.

To evaluate the magnetic state, the coercivity (H_c) of the experimental sample was measured by a ballistic method.

EXPERIMENTAL

Principles of the Method of Determining the True* Heat Capacity. The measurement of the true heat capacity was carried out by a method, similar in principle to the method worked out by Moser [8] and Sykes [9].

The essential part of this method consists in the fact that to the sample, surrounded on all sides by an adiabatic envelope, is continuously transmitted electric energy of known power. The time intervals corresponding to a determined small increase in the temperature of the sample are accurately read at the same time.

The true heat capacity (C_p) of the experimental sample is calculated from the equation:

$$C_p = \left\{ \frac{(Q \pm a \Delta \theta) \Delta \tau}{\Delta t} - K \right\} \cdot \frac{1}{m},$$

where Q is the heat transmitted to the calorimeter (in cal./second), a is the heat exchange coefficient (in cal./second · degree), $\pm \Delta \theta$ is the average deviation from the conditions of adiabaticity (in degrees); Δt is the rise in the temperature of the calorimeter (in degrees), $\Delta \tau$ is the time (in seconds), K is the heat value of the empty calorimeter (cal./degree), and m is the mass of the sample (in grams).

Description of the Calorimeter. The plan of the calorimeter used for the measurement of the true heat capacity, is set forth in Fig. 1. The calorimeter proper, B, consists of two cylindrical barrels tightly entering into each other and readily capable of being withdrawn internally and externally and rigidly fixed in the adiabatic jacket A. Above, the calorimeter was covered with the cover C. All the portions of the calorimeter (with the exclusion of the bottom of the external barrel which was turned out of silver) were made out of heat resistant steel**.

The adiabatic jacket A consisted of a massive silver barrel with a cover consisting of two screw-on portions. In the wall of the lower portion of the barrel were drilled vertical canals in which the thermometric leads leading

* By true heat capacity is understood the average heat capacity measured in a narrow temperature range.

** The composition of the steel (in%) was Cr 25, A 5.5; Ti 0.3; C 0.04 and Fe 69.16.

from the calorimeter B passed. The heat necessary to heat the sample under adiabatic conditions, was supplied with the aid of the heater W.

The heater consisted of a double wound nichrome spiral (resistance approximately equal to 8 ohms) welded to a nichrome stand ($d = 1$ mm), which was hammered out within the calorimeter in plates. The whole system was heated on a tubular electric furnace with a double wound winding (not shown in the figure). The measurement of the temperature was accomplished with the aid of a gold-palladium-platinum thermoelement. The thermoelectromotive force of the thermocouples and the electric energy supplied to the heater were measured by the compensation method (on a Disselhorst compensator). A mirror galvanometer with a sensitivity of $2.5 \cdot 10^{-8}$ A and a coil resistance of 6 ohms served as null instrument.

Subjects of the Investigation and Thermal Treatment. Alloys of the following composition (in atoms%) were investigated:

54.8 Fe,	23.3 Ni,	21.9 Al [alloy (sample)1]
55.7 Fe,	21.0 Ni,	23.3 Al [alloy (sample)2]
35.0 Fe,	25.4 Ni,	39.6 Al [alloy (sample)3].

The first two alloys on the composition diagram of the system Fe-Ni-Al (Fig. 2) [10] are distributed in the two-phase $\beta + \beta'$ region. They go over into the monophasic state at a temperature of approximately 970° [11].

As is well known, it is possible to obtain anomalously high coercivity in alloys of the $\beta + \beta'$ region.

Alloy 3 is found in the β' region. According to the literature data, alloys of this region are not capable of magnetic hardening. The true heat capacity of the final states was studied for each alloy: biphasic, after tempering, monophasic, after quenching. The intermediate states also are of especial interest - the transition state from biphasic to a monophasic melt, -inasmuch as they ensure a maximally high coercivity of the alloy [2].

The tempering of the samples was carried out in a vacuum at 800° for 18 hours with subsequent slow (5 degrees/hour) cooling to 400° . The thermal treatment to obtain a monophasic melt was accomplished by cooling the sample at 1300° in water. The quality of the quenching was controlled by measuring the coercivity

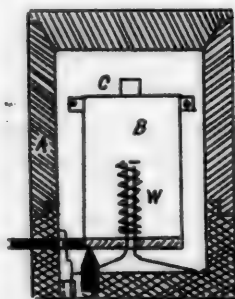


Fig. 1. Plan of the calorimeter.
Explanation in the text.

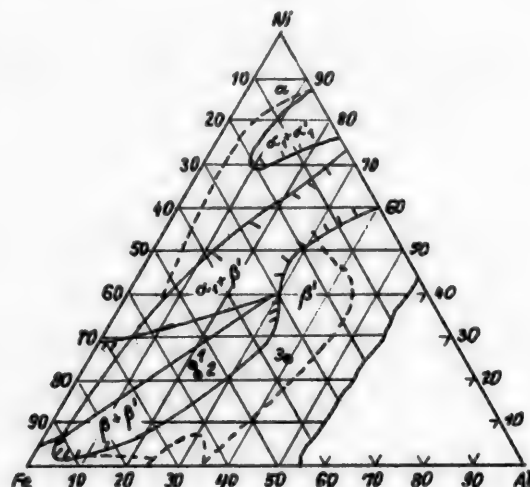


Fig. 2. Composition diagram of the system Fe-Ni-Al, according to Bradley (in atoms%) [10].

of the quenched sample. After quenching, the coercivity of sample 1 amounted to 14 ± 1 oersteds and of sample 2, 50 oersteds. We did not succeed in quenching samples with H_c less in magnitude.

The intermediate states were fixed, on the one hand, by the quenching of a biphasic alloy at various temperatures ($620, 800^\circ$) in water and on the other hand, by a process of repeated adiabatic heatings (in the tempering process) of a sample quenched a minimal coercivity. The heating was repeated until the sample under investigation became maximally coercive ($H_c = 250$ oersteds).

All the measurements of the true heat capacity were carried out up to 700° with a precision of 1-1.5%.

Results of the Measurements of the True Heat Capacity of Sample 1. The results of the measurements of the true heat capacity of sample 1 are set forth in Fig. 3. The curves were drawn with the experimental points obtained for each $2-4^\circ$ taken into account (but the technical causes are not shown in the figure).

The heat capacity of the tempered sample (curve a) increases right up to 500° with a temperature coefficient $\frac{dC_p}{dt}$ that is normal in magnitude. The heat capacity is practically constant in the range 450-550°, changes again in the 600° region with a value of the coefficient $\frac{dC_p}{dt}$ that is normal in magnitude and, finally, above 615° an anomalous change in the heat capacity is observed.

The diminishing of $\frac{dC_p}{dt}$ in the 450-550° regions indicates the presence of a process which is accompanied by a weak exothermic effect (see below).

The behavior of the sample close to 600° can also characterize the presence of a conversion associated with evolution of heat. This conversion can be caused both by further tempering of the melt (inasmuch as carrying out the tempering at 800° can be insufficient) and by coagulation of the already evolved β and β' phases.

The curves b, c and e_1 were obtained after quenching the tempered sample respectively at 620, 800 and 1300° and thus characterize the behavior of a biphasic alloy in the course of assuming the monophasic state.

As is evident, quenching introduces significant changes into the structure of the tempered sample. One must, however, differentiate quenching at 620 and 800° (temperature of existence of the biphasic region $\beta + \beta'$) and at 1300° (temperature of existence of the solid solution β'').

The curves b and c, which characterize the behavior of the biphasic sample after quenching at 620 and 800°, are similar to each other. Each of them indicates the presence in the sample of two conversions which proceed with the evolution of heat: one in the 300-450° region, another in the 450-550° region.

The curve e_1 , which reflects the behavior of the monophasic solid solution β'' , is considerably different from the curves b and c. It has only one minimum in the 300-450° region which is in common with curves b and c. A minimum in the 450-550° region is not observed while a minimum appears in the 580-650° region which is particularly characteristic.

In what follows, the effects pertaining to conversions in the 300-450, 450-550, 580-650° region will be respectively designated as low, middle and high temperature effects.

The curve e_1 completes the series of curves a, b and c which characterize the behavior of the biphasic sample in the process of assuming the monophasic state. At the same time it is the curve of the first heating in the series of curves e_1 , e_2 and e_3 (Fig. 3). These curves were obtained in the process of repeated adiabatic heatings of the sample, quenched at minimal coercivity (approximately equal to 14 oersteds), and therefore characterize the energetic changes in the minimally coercive sample during its transition into a state with high coercivity.

The data of the H_c measurements, before and after each heating, are presented in Table 1.

TABLE 1

No. of heating	Alloy after quenching at 1300° in water			
	1		2	
	H_c (oersted)		H_c (oersted)	
	Before expt.	After expt.	Before expt.	After expt.
1	51.0	233.0	14.1	136.0
2	233.0	250.0	136.0	191.5
3	250.0	250.0 max.	191.5	216.3
4	—	—	216.3	226.0
5	—	—	226.0	226.0 max.

Curves e_2 and e_3 reflect the behavior of a minimally coercive sample, respectively during a second and a third heating.

It follows from the curve of secondary heating, e_2 , that the quenched sample still does not undergo conversion in the 300-450° region. Conversion takes place in the 580-650° region, although the effect of this conversion is expressed considerably more weakly than on curve e_1 .

The fact that a middle temperature exothermic effect, characteristic only of the biphasic state (curves a, b, and c) appears on curve e_2 is very curious.

A high temperature exothermic effect is entirely absent on the curve of the third heating, e_3 , and an effect in the middle temperature region (450-550°) occurs only as on curve e_2 . It is characteristic that the third heating, in contrast to first two heatings, is not accompanied by change in the coercivity (Table 1). This means that curve e_3 reflects the energetic behavior of the maximally coercive sample.

On the basis of the analysis indicated above of the curves of Fig. 3, we can assert that the sample under investigation undergoes (in principle) the same conversions (low temperature, middle temperature and high temperature) regardless of whether it proceeds from the biphasic to the monophasic (curves a, b, c and e_1) or from the monophasic (minimally coercive) to the highly coercive state (curves e_1 , e_2 and e_3).

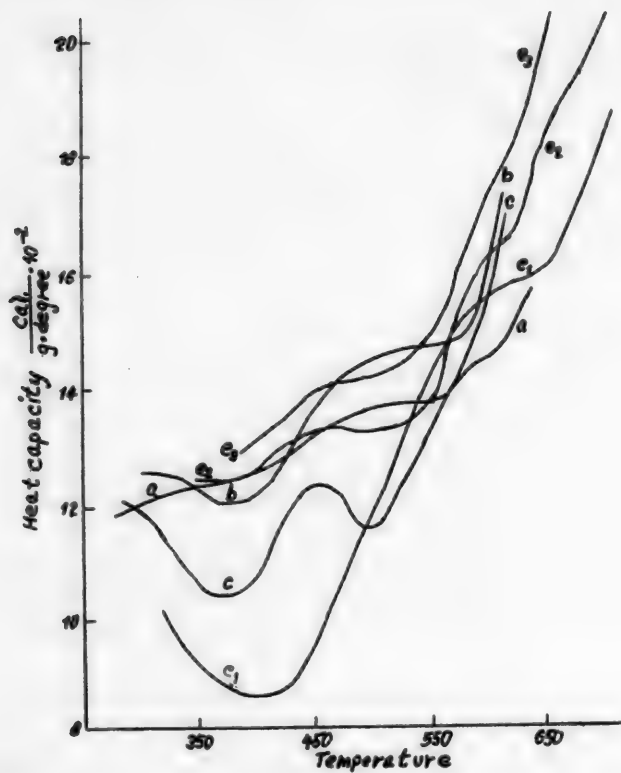


Fig. 3. Curves for the true heat capacity as a function of the temperature of alloy 1 after various heat treatments.

a) After tempering at 800° (18 hours); b) and c) after quenching the tempered sample; e_1 , e_2 , and e_3) curves of the first second and third heatings of a sample, quenched at 1300° in water.

condition for establishing a highly coercive state in Fe - Ni - Al melts.

We link the low temperature exothermic conversion with the effect of supplementary ordering of the high temperature β' phase. The correctness of this assumption is confirmed, in the first place, by the fact that this conversion is strictly localized (300-450°) and in the second place, since this conversion can be observed in a sample by quenching it at various temperatures (620, 800, 1300°), the higher the quenching temperature, the greater the heat effect corresponding to it (curves b , c , and e_1).

In our opinion, the high temperature heat effect is a consequence of decomposition of the high temperature phase into conjugated phases. The following important facts argue in favor of this assertion.

1. A sample, which has undergone high temperature conversion (for example, after the first heating), is capable of undergoing a conversion characteristic of the biphasic state, and specifically middle temperature conversion (curves e_2 , and e_3).
2. The high temperature heat effect occurs only in samples quenched at a temperature at which the monophasic solid solution exists (above 970°). In samples quenched at temperatures at which the biphasic $\beta + \beta'$ region exists, we did not observe such a conversion.

The experimental material obtained does not permit the nature of the middle temperature conversion to be definitely determined. There is no doubt that it is a consequence of processes associated with the formation of conjugated phases from the decomposition of the monophasic solid solution.

Results of the Measurements of the True Heat Capacity of Sample 2. The results of the measurements of the true heat capacity of sample 2 are set forth in Fig. 4. The curves, like those of Fig. 3, are drawn on the basis of the experimental points.

We must now determine which of the indicated conversions is associated with the process of magnetic hardening of Fe - Ni - Al alloys.

Let us return to the comparison of the results of measurements of the true heat capacity (curves e_1 , e_2 , and e_3) and the coercivity of the intermediate states (Table 2) of the sample, obtained in the course of the secondary adiabatic heatings. It follows from this comparison that the energetic conversions in the region of low (300-450°) and middle (450-550°) temperatures do not directly participate in the magnetic hardening of iron-nickel-aluminum alloys. The coercivity of the sample hardly changes while being heated right up to 500°. The increase of H_c occurs in the region of the high temperature exothermic effect, this effect is appreciably weakened with each subsequent heating. A lesser increase in the coercivity (Table 2) corresponds to a lesser exothermic effect. As has already been indicated, on the curve e_3 , which reflects the behavior of a maximally coercive sample, the high temperature exothermic effect is practically absent.

Thus, of the three conversions which have been brought to light, only the conversion in the region of high temperatures (580-650°) is a necessary

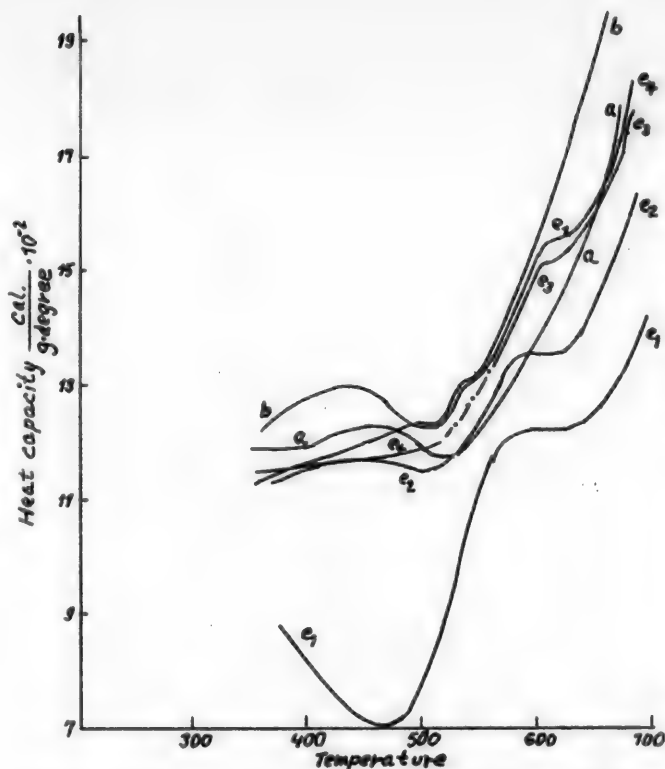


Fig. 4. Curves for the true heat capacity as a function of the temperature of alloy 2 after various heat treatments.

a) After tempering at 800° (18 hrs.); b) after casting; e_1 , e_2 , e_3 , and e_4) the corresponding curves of the first, second, fourth, and fifth heatings of a sample, quenched at 1300° in water.

the total heat effect of the high temperature region exceeds that of sample 1, since the considerable increase in coercive force expected in this connection for sample 2 was not observed. H_c was of the same order for both samples. In the third place, finally, the high temperature conversion effect noted on curve e_4 is not associated, as one was bound to expect, with the change in coercive force (Table 1); curve e_4 as well as curve e_3 , Fig. 3 in fact reflects the state of a maximally coercive sample.

The absence of increase in the coercivity as a result of the fifth heating (curve e_4) of sample 2 should be explained by the presence in it of processes which completely compensate for the action of the high temperature conversion, such as, apparently, coagulation of phases β and β' and the relieving various forms of tension. An appreciable increase in these processes for sample 2 was facilitated by a more prolonged tempering than for sample 1.

Thus, the high temperature conversion is only a necessary, but not a sufficient condition for the establishment in Fe-Ni-Al alloys of maximal coercivity. Conditions, in which there are processes which compensate for the action of the high temperature conversion, must be acknowledged, apparently, as sufficient. We assume that the conditions of magnetic hardening during continuous quenching of the sample at a certain critical rate approach such conditions. This thermal treatment, as is well known, permits one to achieve maximal coercivity. It is therefore of interest to return to the analysis of curve b , Fig. 4, which reflects the energetic behavior of a highly coercive (approximately 370 oersteds) sample obtained by casting.

Curve b is characterized by one heat effect in the middle temperature region (450-550°); the high temperature heat effect is actually absent. In form, curve b brings to mind the curve (e_3 of Fig. 3) of the highly coercive sample 1, which, as we demonstrated, is, in comparison with sample 2, less subject to the influence of processes which compensate for the action of high temperature conversion.

The similarity of curves b and e_3 also argues in favor of the conclusion that no kind of difference (in principle) between the structures of the highly coercive samples, obtained under the conditions of quenching and tempering, and in

- e_3 and e_4 are respectively the curves of the fourth and fifth heatings. The curve of the third heating is not shown on Fig. 4.
- The rates of heatings were identical.

By analogy with sample 1, curve a characterizes the energetic behavior of a tempered sample, while curves e_1 , e_2 , e_3 , e_4 reflect the energetic changes in a sample, quenched at minimal coercivity (50 oersteds) in the course of the secondary adiabatic heatings.

It can readily be seen that curves a and e_1 do not qualitatively differ from the corresponding curves of sample 1. The differences which are present amount only to the fact that the heat effects caused by the low temperature and high temperature conversions are more sharply expressed on the curves of sample 2.

Energetic changes analogous to those of sample 1 are also reflected on curves e_2 , e_3 and e_4 . Sample 2 also did not undergo conversion in the low temperature region on second heating (curve e_2); the conversion in the high temperature (580-650°) is retained and conversion is observed in the middle temperature region (450-550°). Each subsequent heating (curves e_1 , e_2 , e_3 , e_4) is characterized by a high temperature heat effect which is weaker in comparison with the preceding and a smaller increase in the value of H_c (Table 2).

However, the kinetics of the decomposition of the high temperature solid solution β' , and consequently, the conditions of the magnetic hardening of samples 1 and 2 is appreciably different. In the first place, the maximum possible coercivity for sample 2 is reached with the least speed (four heatings as against two ** for sample 1); in the second place,

the process of continuous cooling, is observed.

Curves of the True Heat Capacity of Sample 3. Sample 3 (in composition 39.6 atoms % Al, 25.4 atoms % Ni) is decomposed in the monophasic region of Bradley (Fig. 2).

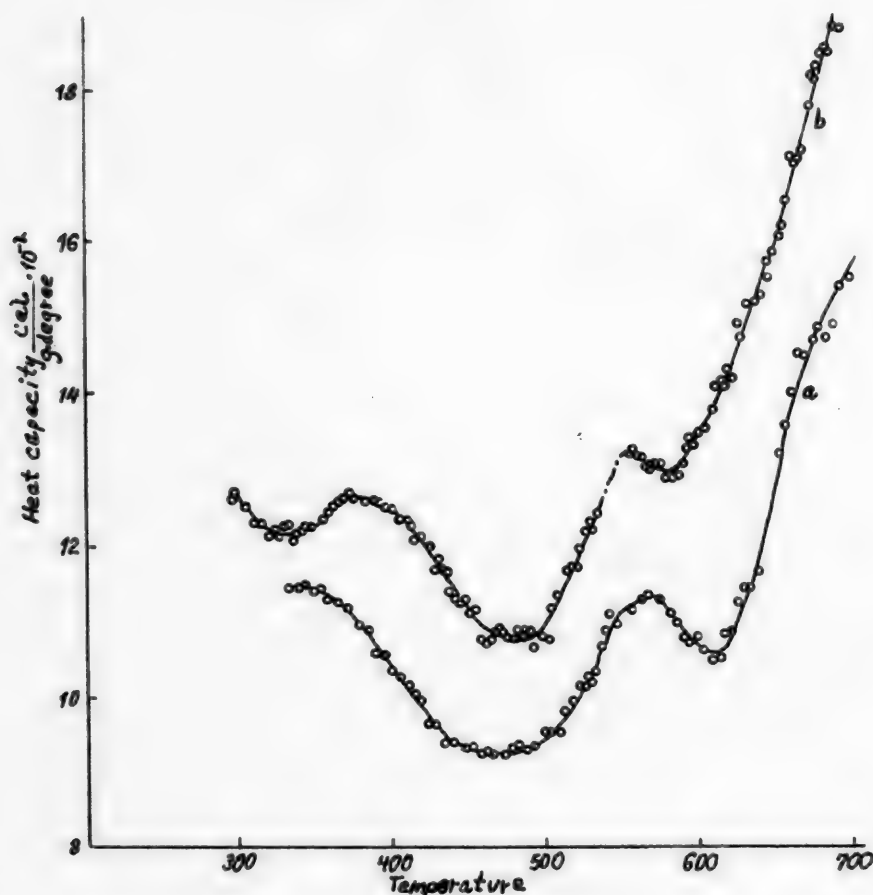


Fig. 5. Curves for the true heat capacity as a function of the temperature of melt 3.
a) Sample quenched at 1300° in water; b) sample tempered at 800° (length of heating 5 hours).

The curves for the true heat capacity of sample 3 are set forth in Fig. 5. Curve a was obtained by heating the sample, quenched at 1300° in water, curve b with the same sample, but held at 800° for a duration of 5 hours and quenched at this temperature in water.

The shape of curve a brings to mind the curves for other samples quenched at 1300° in water (curves e₁ Fig. 3 and 4). In accordance with these, the heat effect in the 350-500° region should be ascribed to a supplementary ordering of the high temperature β' phase and the effect observed in the 550-660° region, to its decomposition. The given hypothesis is found to be in complete agreement with the results of the measurements of the coercivity. Prior to heating the coercivity of the sample was determined to be 4 oersteds and, after heating it rose to a value of 140 oersteds. We assume that when quenched, sample 3 undergoes precipitation hardening with evolution of the same excess phase as samples 1 and 2.

Curve b also brings to mind one of the curves of biphasic state of the alloys under consideration. In the low temperature region (up to 550°) it was qualitatively close to curve c of Fig. 3, since it is characterized by heat effects which are caused by low and middle temperature conversions. The quantitative differences in the comparable heat effects of curves b and c, and also the displacement of the minimums of the heat effects on curve b in the direction of lower temperatures argues only for differing compositions and quantitative ratios of the decomposed phases.

In the high temperature region, curve b is close in its shape to curve e₄ (Fig. 4). As in the latter, curve b reflects the behavior of a maximally coercive sample (H_c before and after heating is equal to 158 oersteds) and at the same

TABLE 2

Alloy 1 after quenching at 1300°						Alloy 2 after quenching at 1300° in water					
No. of heat-ing	H _c (oersteds) at the given temp.					No. of heat-ing	H _c (oersteds) at the given temp.				
	Room	515°	620°	703°	Increase in H _c		Room	515°	620°	703°	Increase in H _c
1	51.0	51.0	58.00	190.0	30.0	1	14.4	No change	14.9	86.5	49.5
2	51.0	55.0	69.00	220.0	12.7	2	14.4		18.0	136.0	23.7
3	51.0	56.7	74.16	232.7		3	14.4		20.0	159.7	
						4	14.4		24.0	178.0	18.3

times indicates the presence in sample 3 of high temperature conversion. Apparently, the magnetic hardening of this sample, like that of sample 2, was subject to processes which compensate for the action of the high temperature exothermic effect.

Thus, the behavior of sample 3 does not correspond to the monophasic composition plotted on the composition diagram of the Fe-Ni-Al system (Fig. 2). The given diagram, in spite of the changes which were introduced in 1951 [12], requires further refinement.

SUMMARY

1. The true heat capacity of tempered, quenched and highly coercive melts was studied:
 - a) in the $\beta + \beta'$ region, with a composition of 54.8 atoms % of Fe, 23.3 atoms % of Ni, 21.9 atoms % of Al, and 55.7 atoms % of Fe, 21.0 atoms % of Ni, 23.3 atoms % of Al; and b) in the β' region with a content of 35.0 atoms % of Fe, 25.4 atoms % of Ni; 39.6 atoms % of Al.
2. The energetic changes in the course of reaching iron-nickel-aluminum alloys of high coercivity state were considered.
3. The presence of three exothermic conversions in the 300-450, 450-550 and 580-650° region was noted.
4. It was established that a conversion in the 580-650° region was associated with processes of magnetic hardening of iron-nickel-aluminum alloys.
5. It was shown that the boundaries of the $\beta + \beta'$ region of the composition diagram of the Fe-Ni-Al system requires further refinement.
6. The region of precipitation hardening of Fe-Ni-Al alloys was rendered more precise; specifically, it was placed above 550°. Processes were observed in the sample which were accompanied by low and middle temperature effects and which did not directly participate in the magnetic hardening of these melts.
7. The experimental data do not permit us to note any differences in principle between the energetic states of the highly coercive samples obtained in the process of quenching and tempering and under conditions of continuous cooling.

LITERATURE CITED

- [1] V. S. Meskin. Ferromagnetic Alloys (1937).
- [2] B. G. Livshits. High Coercivity Alloys (1945).
- [3] S. V. Vonsovsky and Ya. S. Shur. Ferromagnetism (1948).
- [4] O. S. Ivanov and Yu. M. Kazimirov, Proc. Acad. Sci. USSR, 81, 35 (1951).
- [5] Yu. L. Skakov, Proc. Acad. Sci. USSR, 79, 69 (1951).
- [6] N. N. Bulnov and R. M. Leriman, Proc. Acad. Sci. USSR, 79, 69 (1951).
- [7] W. Dannöhl, Arch. Eisenhüttenwesen, 15, 321 (1942).
- [8] H. Moser, Phys. Z., 37, 737 (1936).
- [9] C. Sykes, J. Inst. Met., 59, 257 (1936).
- [10] A. I. Bradley and A. Taylor, Pr. roy. Soc., A., 166, 353 (1938).

[11] O. S. Ivanov, Bull. Inst. Sect. Phys. Chem. Anal., Acad. Sci. USSR, 19, 503 (1949).

[12] A. I. Bradley, J. Iron. Steel. Inst., No. 3, 168, 1951.

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INVESTIGATIONS IN THE FIELD OF POLYTHIONIC ACIDS

IV. SULFURIZATION OF HEXATHIONIC ACID

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Hexathionic acid, formed as a result of the reaction of free thiosulfuric acid and hydrogen sulfide according to the equation



adds a certain quantity of elementary sulfur and, thus, is partially converted into polythionic acids of a higher degree of sulfurization. We recently succeeded in showing that in the solutions obtained as a result of the indicated reaction, octathionic acid is present [1]. However, its quantity in such solutions is very small, since the sulfurization of hexathionic acid, i.e., the reaction of the products of reaction 1 proceeds on a very limited scale: the average content of sulfur in the molecule of the polythionic acid obtained does not reach more than 6.5.

In the present work we have set ourselves the task of accomplishing the sulfurization of hexathionic acid on as large a scale as possible and of obtaining solutions containing predominantly acids with more than six sulfur atoms in the molecule.

EXPERIMENTAL

1. Preparation of solutions of polythionic acids with an average number of sulfur atoms in the molecule, \bar{n} , equal to approximately 7. The first method by which it proved to be possible to accomplish the task indicated above, involved carrying out reaction (1) in concentrated hydrochloric acid in the presence of sulfurous acid. The optimal molar ratio of the starting materials — thiosulfate : sulfide : disulfite was 3:1:2.

150 ml of concentrated (10.5-12N) hydrochloric acid was cooled in a flask with a ground stopper to a temperature below 10°. A solution of 16 millimoles of NaHSO_3 in 20 ml of water was carefully poured into this acid, and the flask was at once covered. In another vessel a solution of 24 millimoles of $\text{Na}_2\text{S}_2\text{O}_3$ in 20 ml of water was stirred with a concentrated solution of sulfide containing 8 millimoles of KHS or Na_2S . This mixture was carefully distributed from a submerged pipet into the mixture of hydrochloric acid and bisulfite. On shaking a white crystalline precipitate (NaCl or KCl) at once appeared, and quickly settled out. After several minutes an opalescence — the beginning of sulfur evolution — appeared. In the course of 15-20 minutes the reaction mixture was diluted in a measuring flask with 5 N hydrochloric acid to 250 ml, corked and left in a cooled place (approximately 10°). After 15-16 hours a sample was taken from the transparent upper layer of the solution to determine the hydrosulfuric acid. The remaining mixture was filtered through a dry weighed filter into a dry vessel. The sulfur which was filtered off was dried in a desiccator and weighed and the mother liquor was subjected to analysis for sulfur compounds [2].

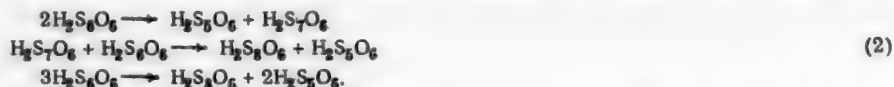
It is evident from the experimental data (Table 1) that a solution of polythionic acid is formed in this way, the composition of which approximately corresponds to that of heptathionic acid; therefore one could expect that heptathionic acid in the form of its benzidine salt could be obtained from such a solution.

We carried out the fractional precipitation of the polythionic acids with benzidine chloride from the solutions of experiments 4 - 7 and determined the average number of sulfur atoms in the molecule of the benzidine salt preparations obtained [1]. It is evident from the data presented (Table 2) that fraction I of the precipitate consisted of octathionate in all cases and II, of the hexathionate of benzidine. We did not succeed in obtaining heptathionate.

It follows from this that the solutions with \bar{n} approximately equal to 7 obtained by the above method, primarily contain octathionic and hexathionic acid, in approximately equal quantities, but do not contain appreciable quantities of heptathionic acid. The latter, evidently, if it exists in general, must be in a very stable equilibrium with both other acids.

It is interesting that fraction III of the benzidine salt precipitate again consists of octathionate. This fraction is evolved after addition to the mother liquor from Fraction II of excess benzidine chloride and being left to stand for

3 - 4 days in a cooled place. It follows from this that after eliminating a considerable portion of the octathionic acid (fraction I of the benzidine salt) a slow accumulation of the latter proceeds anew in the solution, probably via redistribution of sulfur between molecules of polythionic acids, for example, according to the equations:



The basic reaction leading to the formation of polythionic acids under the conditions described above should be considered reaction (1), since the number of moles of polythionic acids found in all cases was equal to about one third of the number of moles of thiosulfate taken or somewhat less. Consequently, the polythionic acid which is primarily formed here, appears to be hexathionic acid. Sulfurous acid undoubtedly participates in its sulfurization to octathionic acid, since in the absence of the latter this sulfurization proceeds only on a small scale among the starting materials [1].

TABLE 1

Products of the Reaction of 24 Millimoles of $\text{Na}_2\text{S}_2\text{O}_3$, 8 Millimoles of KHS and 16 Millimoles of NaHSO_3 in Concentrated HCl

Experiment No.	Content (in millimoles) of			Content of elementary sulfur (in mg-atoms)	Number of sulfur atoms \bar{n}
	$\text{H}_2\text{S}_n\text{O}_6$	$\text{H}_2\text{S}_m\text{O}_6$	SO_2		
1	7.05	1.50	13.24	5.78	7.25
2	8.13	1.25	10.00	—	7.00
3	7.50	5.00	12.70	5.42	6.83
4	7.87	0.50	15.28	2.60	6.84
5	6.56	1.25	14.53	5.20	7.06
6	6.69	1.25	14.66	4.25	7.07
7	8.12	—	14.06	—	6.90

TABLE 2

Average Number of Sulfur Atoms (\bar{n}) in the Molecule of Benzidine Polythionates (Experiments 4-7) after Fractional Precipitation

Experiment No.	Number of sulfur atoms		
	Fraction		
	I	II	III
4	8.1	6.1	8.0
5	8.0	6.2	8.0
6	8.1	—	—
7	8.2	—	—

Sulfurous acid here plays, evidently, the role of sulfur carrier: it first adds elementary sulfur, freed as a result of reaction (1),



while the thiosulfuric acid which is formed gives up, under the given conditions of acidity, a sulfur atom to the hexathionic acid

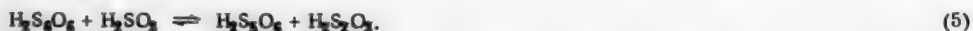


The latter reaction probably proceeds in two stages, i.e., via the unstable heptathionic acid.

Reaction (3) can proceed from left to right under the conditions of our experiments, since the free thiosulfuric acid has a considerably greater stability in relation to the ordinary decomposition with elimination of sulfur [3]. The remarkably high hydrogen ion concentration also appears to be a prerequisite for the formation of octathionic acid according to equation (4), i.e., the displacement of this equilibrium is to the right.

Experiments 8 and 9, carried out under completely analogous conditions, but with the use of 2 N hydrochloric acid in place of concentrated hydrochloric acid (Table 3) illustrate this role of the hydrogen ion concentration.

Here too, the primary reaction in the formation of polythionic acid is undoubtedly the reaction of thiosulfuric acid with hydrogen sulfide according to equation (1), since the number of moles of polythionic acid formed amounts to around one third of the number of moles of thiosulfate taken and is almost equal to the number of moles of sulfide taken. But here, in place of the sulfonation of hexathionic acid, its so-called sulfite decomposition to pentathionic acid occurs according to the equation



Inasmuch as the thiosulfuric acid here regenerated is unstable in dilute hydrochloric acid, we find considerably more elementary sulfur in these experiments than equation (1) requires, and almost all the initial sulfurous acid.

TABLE 3

Products of the Reaction of 48 Millimoles of $\text{Na}_2\text{S}_2\text{O}_3$, 16 Millimoles of KHS and 32 Millimoles of NaHSO_3 in 2N HCl

Experiment No.	Content (in millimoles) of			Content of elementary sulfur (in mg-atoms)	Number of sulfur atoms n
	H_2SnO_6	$\text{H}_2\text{S}_2\text{O}_3$	SO_2		
8	15.0	7.0	28.7	26.6	5.20
9	15.6	3.1	30.3	26.9	4.95

2. Preparation of solutions of octathionic acid. In the experiments described above, sulfuration of hexathionic acid proceeds due to the elementary sulfur freed as a result of reaction (1); therefore the heptathionic acid or the mixture which we obtained of equivalent quantities of octathionic and hexathionic acids here represent the theoretical limit of sulfuration.

With the object of exceeding this limit we attempted to accomplish in one and the same solution the two basic reactions - reaction (1), giving hexathionic acid and sulfur and simultaneously the reaction of hydrogen sulfide with sulfurous acid.



We started at the same time on the assumption that the additional quantity of sulfur which reaction (6) would give could, although partially, add to the hexathionic acid which was being formed as a result of reaction (1).

The experimental data (Table 4) show that, starting with a molar ratio of the reagents - thiosulfate : sulfide : bisulfite of 6:7:5, with a small excess of bisulfite, * we succeeded in obtaining a solution containing almost all the sulfur of the starting materials (up to 98%) in the form of polythionic acids with an average number of sulfur atoms in the molecule $n = 8$.

TABLE 4

Reaction of Thiosulfate, Sulfide and Bisulfite with Hydrochloric Acid

Experiment No.	Amount taken of				Concentration of HCl (N)	Volume of the mixture (in ml)	Reaction products				Number of sulfur atoms n
	$\text{Na}_2\text{S}_2\text{O}_3$	NaHS	NaHSO_3	HCl (in ml)			H_2SnO_6	$\text{H}_2\text{S}_2\text{O}_3$	SO_2	S (in mg-atoms)	
	(In millimoles)						(In millimoles)				
10	24.0	27.75	22.85	300	1.6	500	11.50	0.50	0.69	0.63	7.97
11	24.0	27.75	22.85	300	1.6	500	10.75	1.00	0.62	1.95	7.91
12	24.0	28.00	25.00	300	2.0	500	12.25	0.25	3.06	1.17	7.93
13	120.0	138.80	105.80	700	3.4	1000	59.0	3.50	2.75	Traces	8.00
14	120.0	140.00	116.00	700	3.4	1000	59.5	3.00	2.40	Traces	8.00
15	120.0	138.80	105.80	700	3.4	1000	59.9	0.50	1.70	Traces	8.00
16	60.0	70.00	56.00	300	5.0	500	29.4	4.00	1.80	Traces	7.80
17	60.0	70.00	52.40	300	5.0	500	29.5	0.00	1.75	Traces	8.00
18	60.0	70.00	58.00	300	5.0	500	29.0	3.00	4.25	Traces	7.90

The experimental methods of these experiments were analogous to those described above for experiments 1-9 with only this difference, that here it was not necessary to let the reaction mixture stand for a prolonged time, since sulfur was almost not evolved at all or was evolved only in a small quantity and quickly precipitated. In this case it proved expedient to carry out the reaction not in a concentrated but in moderately dilute hydrochloric acid solution. The dilution of the reaction mixture could be carried out with water in a measuring flask. At the optimal concentration of hydrochloric acid (3.4-5 N, experiments 13-18), sulfur was hardly evolved at all, and sometimes only a light opalescence appeared while the solution acquired a yellowish color.

Precipitation of polythionic acid from these solutions with benzidine chloride gave benzidine octathionate (Table 5); we did not succeed in obtaining any other polythionates of benzidine by fractional precipitation in this case. It follows from this that these solutions predominantly contain octathionic acid, which has considerable stability under the given conditions.

The circumstance, that solutions of octathionic acid prepared under optimal acidity conditions (3.4-5 N HCl, experiments 13-18) remain transparent for 4-5 hours, and, after 2-3 days at a temperature not exceeding 10° , evolve only an insignificant quantity of sulfur, also indicates the comparative stability of octathionic acid.

The number of moles of octathionic acid formed in these experiments exceeds by one third the number of moles of thiosulfate taken. Consequently, the formation of polythionic acid here proceeds not only via reaction (1), but also as a result of the reaction of hydrogen sulfide with sulfurous acid, as in the well known Vakenroder solution. The general

* Excess bisulfite was necessary in view of the fact that at the time of the experiment a small quantity of sulfur dioxide volatilized.

i.e., the total process can be expressed by the equation:



Our experimental data, in particular the results of experiments 13-18, carried out at optimal solution acidity, are found to be in entire agreement with this equation: the number of moles of octathionic acid found is almost exactly equal to half the number of moles of the thiosulfate taken and almost all the sulfur of the starting materials is found in the form of this acid.

TABLE 5
Number of Sulfur Atoms
in the Benzidine Polythion-
ates from Experiments 16-18

Experiment No.	n
16	8.0
17	8.02
18	8.0

Equation (7) can be obtained by the addition of a series of simple equations, which still express well known reactions; specifically, equations (1), (3), (4), (6), and also:



and



The mechanism of reaction (1) has already been analyzed by us previously [1].

A somewhat simpler overall expression for the formation of octathionic acid from these same substances can be obtained by another combination of these same equations:



The quantitative completion of the reaction according to this equation, however, can not be accomplished except at an initial ratio of the reacting substances of 5:4:2, since the evolution of considerable quantities of sulfur can not be successfully avoided.

SUMMARY

1. The reaction of thiosulfuric acid with hydrogen sulfide in concentrated hydrochloric acid in the presence of sulfurous acid leads to the formation of a solution of polythionic acid which corresponds in its composition to heptathionic acid, but which consists of a mixture of octathionic and hexathionic acids.

2. Thiosulfuric acid, hydrogen sulfide and sulfurous acid react almost quantitatively in moderately dilute hydrochloric acid to form octathionic acid.

LITERATURE CITED

- [1]. I. V. Yanitsky and I. N. Valanchunas, J. Gen. Chem., Supplement I, 732 (1953).
- [2]. A. Kurtenacker and A. Czernotzky, Z. allg. anorg. Chem., 174, 179 (1928).
- [3]. J. Janickis, Z. allg. anorg. Chem., 234, 193 (1937).
- [4]. H. Stamm and M. Goehring, Z. allg. anorg. Chem., 242, 413 (1939).

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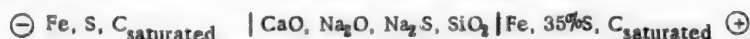
CERTAIN THERMODYNAMIC PROPERTIES OF SULFUR IN LIQUID IRON-SULFUR ALLOYS SATURATED WITH CARBON

N. A. Vatolin and O. A. Esin

The thermodynamic properties, in particular the activity, of sulfur dissolved in liquid iron and the influence on it of various elements (C, Cu, Si, P, Al and others) have been determined by a number of investigators from data of the chemical equilibrium of an alloy with the gaseous phase [1]. It was discovered that the Fe-S system is characterized by positive deviations from the laws of ideal solutions. Additions of carbon intensify these deviations; this is explained by the appearance of a region of stratification of the liquids. It turned out, for example that at 2.3% C the coefficient of activity of sulfur is doubled while in alloys saturated with carbon, it is increased 6 times [2].

It was of interest to follow the behavior of sulfur in alloys saturated with carbon, in the entire Fe-FeS composition range, since no such investigations have been carried out. With this object, the method of electromotive forces, which has thoroughly proved its value in sulfide systems [3,4] was used.

In following this method, the concentration chain which follows was set up



The content of sulfur at one of the electrodes was varied from experiment to experiment from 0.048 to 33%, while it was kept constant and equal to 35% S at the other electrode.

Alloys of varying composition were prepared from synthetic cast iron (4.4% C, 0.08% Mn, 0.1% Si, 0.03% S), the material of the comparison electrode was (35% S, 0.1% Si, 0.2% Mn, 0.15% C). They were fused at a temperature of 1250° in a graphite crucible under a layer of wood charcoal while being constantly stirred. The concentration of carbon in the alloys containing up to 0.71% S, varied from 4.5 to 3.5% C and did not markedly differ from that calculated according to the empirical [5] formula

$$[\%C] = 1.19 + 0.00262t - [\%S] \{1.67 - 0.001 \cdot (t - 1200)\}. \quad (1)$$

An alloy of composition: 72% SiO₂, 17% Na₂O, 9% CaO, 2% Na₂S, served as electrolyte. It was obtained by fusing glass with sodium sulfide in a graphite crucible. The experiments were carried out at a temperature of 1250°. The electrolyzer was made of refractory clay. The construction of the electrolyzer and also the methods of the measurements were similar to those previously described [6].

Since the activity of carbon was identical at both electrodes, while there were no iron ions in the electrolyte, the only process which determined the potential was the conversion of sulfur:



In this connection the electromotive force of the element must be determined only by the ratio of sulfur in the alloys:

$$E = \frac{RT}{2F} \ln \frac{a_S}{a_S} \quad (3)$$

We can calculate the value of a_S with the aid of equation (3) if we assume that in the most dilute solution the activity is equal to the atomic fraction ($a_S^0 = N_S^0 = 0.00072$). Then

$$-0.460 = -E = 0.1523 \log \frac{0.00072}{a_S} \quad (4)$$

The changes in free energy during the transition of a gram atom of sulfur from a more concentrated alloy to a dilute alloy is also calculated from the observed values for the electromotive forces:

$$-\Delta F = 2 \cdot 23060 E. \quad (5)$$

The results obtained are set forth in Table 1 and presented in the figure. It is evident from the latter that the isotherm of electromotive forces has 3 portions. At the same time the two receding curves correspond to homogeneous alloys while the horizontal branch corresponds to the stratification interval.

The limits of stratification found by us were to 0.75 and 27.5% S, which is in agreement with the data obtained by other methods. Thus, on the fusibility diagram of the system Fe-S-C they correspond to 0.8 and 29.5% S [7] at 1100°.

TABLE 1

Dependence of the Electromotive Force on the Composition of the alloy at 1250°

Composition of the alloy in % by weight		Atomic fraction N_S	E (mV)	a_S	γ_S	$-\Delta$ (cal/g-at.)
S	C					
0.048	4.4	0.00072	460	0.00072	1.0	21200
0.06	4.4	0.00090	450	0.00084	0.93	20750
0.14	4.2	0.0021	400	0.0018	0.84	18450
0.31	4.0	0.0047	350	0.0039	0.81	16150
0.71	3.3	0.0111	295	0.0087	0.79	13600
29.0	0.2	0.41	190	0.043	0.104	8770
30.0	0.2	0.43	140	0.091	0.287	6460
33.0	0.15	0.46	60	0.306	1.665	2770
35.0	0.15	0.48	0	0.758	1.57	0

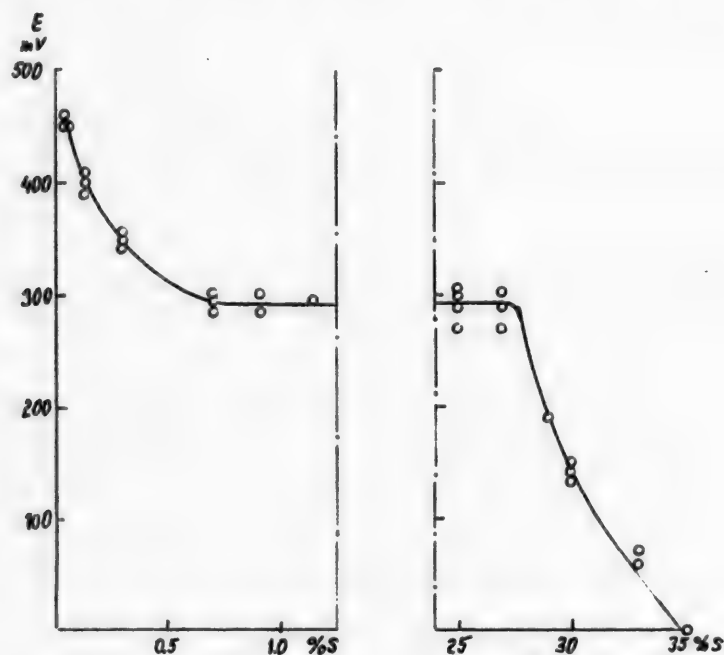


Fig. 1. Dependence of the electromotive force on the content of sulfur in the liquid alloy Fe-S-C_{saturated} at a temperature of 1250°. (The abscissa of the left portion of the curve is on a different scale from that of the right.)

It follows from the data of Table 1 that up to the point when stratification begins, the coefficient of activity of sulfur (γ_S) falls with increase in its concentration. Such a course of the changes of γ_S qualitatively coincides with that found by another method for alloys of Fe-FeS at 1600° [1]. However, in our case the fall in the activity coefficient occurs more rapidly (from 1 to 0.79 instead of 0.9). This is due, probably to the lower temperature of our experiments (1250°).

The activity of sulfur (a_S) in alloys compares with its greater content according to the data of Volsky and Agracheva [8]. The latter determined the equilibrium pressure P_{S_2} over solutions of FeS in Fe at a temperature of 1200°.

Taking as standard state an alloy containing 35% S, i.e., placing $a_S^0 = 1$ for it, we find the activity of sulfur from their data according to the equation

$$\log a_S = \frac{1}{2} (\log P_{S_2} - \log P_{S_2}^0). \quad (6)$$

The activities calculated by this method are compared in Table 2 with those determined from the electro-

motive forces. The agreement is quite good, particularly if one takes account of the defects of both methods of measurements.

In the last columns of Table 2 the activity coefficients calculated from the formula proposed by Samarin and Shvartsman [9] are presented:

$$\gamma_S^I = \frac{1}{1 - 5(N_C + N_S)} \quad (7)$$

In it N_C and N_S are the atomic fractions of carbon and sulfur. For convenience in comparing them with γ_S coefficients obtained from the electromotive forces, all γ_S^I values are divided by 8.7. The data of Table 2 confirm the conclusions of Samarin and Shvartsman [9], that equation (7) can not be applied to alloys containing more than 3% carbon.

TABLE 2

Comparison of a_S and γ_S Calculated from Different Data

Content of S (in %)	a_S^*		Content of S (in %)	γ_S^{**} (from the emf)	γ_S^* cal- culated according to equation (7)	$\gamma_S = \frac{\gamma_S^*}{8.7}$
	Calculated accord- ing to equation (6)	Accord- ing to the emf				
35.0	1	1	0.048	1.0	8.7	1
33.0	0.525	0.404	0.06	0.93	8.78	1.01
30.0	0.144	0.120	0.14	0.84	6.85	0.79
29.0	0.102	0.060	0.30	0.81	6.02	0.69
			0.71	0.79	3.85	0.44

* The standard state alloy contained 35% S, $a_S^0 = 1$.

** The standard state alloy contained 0.048% S and 4.4% C, $\gamma_S^0 = 1$.

SUMMARY

1. Measurements of the electromotive forces of a concentrated element, the electrodes of which consisted of liquid alloys of iron with sulfur, saturated with carbon, were carried out.
2. The activity and activity coefficients of sulfur in these alloys were calculated and the change in free energy in the transition of a gram atom of sulfur from one solution to another was also determined.
3. The results obtained satisfactorily agree with the data found by other methods (fusibility diagram, chemical equilibria).

LITERATURE CITED

- [1]. Ch. U. Sherman and J. Chipman. Problems of Contemporary Metallurgy, No. 1 (7) (1953).
- [2]. I. P. Morris and R. C. Buehl, J. Metals, 188, 317 (1950).
- [3]. O. A. Esin and I. T. Sryvalin, J. Phys. Chem., 25, 1503 (1951).
- [4]. I. T. Sryvalin and O. A. Esin, J. Phys. Chem., 26, 371 (1952).
- [5]. D. A. Spratt and J. A. Kitchener, J. Iron and Steel, 172, 4, 383 (1952).
- [6]. O. A. Esin and L. K. Gavrilov, Bull. Acad. Sci. USSR, Div. Tech. Sci., No. 8, 1234 (1951).
- [7]. R. Obergröffer, Technical Iron. Metallurgy Press, p.93 (1940).
- [8]. A. N. Volsky. Fundamentals of the Theory of Metallurgical Alloys, Metallurgy Press, p 18 (1943).
- [9]. A. M. Samarin and L. A. Shvartsman, Bull. Acad. Sci. USSR, Div. Tech. Sci., No. 3, 407 (1951).

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CALCULATION OF THE VISCOSITY OF BINARY SYSTEMS. I

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In the works of Panchenkov [1,2] a formula for the dependence of viscosity of liquids on the temperature is introduced. The author indicates that this formula can be used for finding the dependence of the viscosity of mixtures on the composition. The formula of Panchenkov has been verified for a large number of liquids, and also for 5 binary systems [1,3].

We have collected much experimental material on the viscosity of binary systems. It was of interest to investigate how the calculated values for the viscosity would agree with our experimental data.

In the calculations of the viscosity of pure components and their mixtures we used the somewhat modified Panchenkov formula [1]:

$$\eta = 4 A \rho^{4/3} T^{1/2} \operatorname{Sh}^2 \frac{E}{2RT},$$

which is more convenient in the calculations.

In the present article the calculated values for the viscosity of the system dichloroethane-methyl alcohol (Table 1), dichloroethane-ethyl alcohol (Table 2), dichloroethane-propyl alcohol (Table 3), dichloroethane-butyl alcohol (Table 4) and dichloroethane-isoamyl alcohol (Table 5) are presented.

The experimental data on the viscosity and density of the systems enumerated have been published elsewhere.

In Tables 1-5, along with the calculated values for the viscosity, the percentage deviations of the calculated viscosity value from the experimental value ($\Delta \eta\%$), the value of the bond energy of a molecule of the mixture (E_c) and the logarithm of the constant A_s , as a function of the composition of the mixture, are given.

For calculating the values of $\log A_s$ we used the experimental data for the viscosity at 60° [4], and consequently the calculated values for the viscosity at this temperature are not presented in Tables 1-5.

It is evident from the data of Table 1.5 that the calculated values for the viscosity are in excellent agreement with the experimental data. The average deviation of the experimental from the calculated values for the viscosity is only in excess of 1% in a few cases.

It is of interest to note that the functional dependence between the bond energy of the molecules of the mixture and the composition of the mixture can be used to construct a physico-chemical analytical composition-property diagram. The dependence of the bond energy of the molecules on the composition in the system methyl alcohol-dichloroethane (Table 1) is expressed by a curve which passes through a maximum (Fig. 1). The components of this system react chemically [4], which leads to an increase in the bond energy of the molecules and the appearance of a maximum on the curve.

In Figure 2, the "bond energy-composition" curves of the system ethyl alcohol-dichloroethane (curve I), propyl alcohol-dichloroethane (curve II), butyl alcohol-dichloroethane (curve III) and isoamyl alcohol-dichloroethane (curve IV) are presented in the form of a single diagram. The components of these systems do not react chemically [4]. The "bond energy-composition" curves are convex toward the abscissa axis and the convexity increases from the system ethyl alcohol-dichloroethane to the system isoamyl alcohol-dichloroethane. The extent of association of the alcohols diminishes in the same sequence.

SUMMARY

1. Viscosity calculations for five binary systems were carried out according to Panchenkov's formula. Excellent agreement was obtained between the calculated values for viscosity and the experimental data.

TABLE 1

The System Methyl Alcohol - Dichloroethane

CH ₃ OH (moles %)	Viscosity, calculated according to Panchenkov's formula						E ₁₂ = 2851.3	
	30°		40°		50°		E _c	log A _s
	$\eta \cdot 10^3$	$\Delta\eta, \%$	$\eta \cdot 10^3$	$\Delta\eta, \%$	$\eta \cdot 10^3$	$\Delta\eta, \%$		
0.00	7.249	-0.10	6.423	+0.63	5.716	-0.14	2197.0	$\bar{6}.93338$
15.68	6.732	+2.23	5.895	+2.13	5.217	+0.93	2378.8	$\bar{6}.78193$
23.69	6.503	+1.46	5.672	+1.36	4.999	+0.18	2453.7	$\bar{6}.72257$
42.17	6.239	+1.86	5.395	+1.45	4.741	+0.68	2579.9	$\bar{6}.64227$
53.74	6.014	-0.30	5.211	-0.31	4.548	-0.74	2625.6	$\bar{6}.61585$
62.21	5.974	+0.64	5.146	+1.02	4.297	-0.02	2643.0	$\bar{6}.61943$
69.06	5.821	-0.05	5.044	+0.78	4.389	-0.75	2647.0	$\bar{6}.62697$
79.82	5.665	-0.54	4.920	+0.10	4.285	-0.88	2635.5	$\bar{6}.66023$
83.93	5.639	+0.39	4.888	+0.74	4.272	+0.40	2625.2	$\bar{6}.68225$
91.20	5.513	+0.46	4.777	+0.32	4.190	-0.21	2599.2	$\bar{6}.72558$
100.00	5.228	-0.02	4.538	-0.02	3.990	-0.84	2554.3	$\bar{6}.78714$

TABLE 2

The System Ethyl Alcohol - Dichloroethane

C ₂ H ₅ OH (in moles %)	Viscosity, calculated according to Panchenkov's formula						E ₁₂ = 2683.7	
	30°		40°		50°		E _c	log A _s
	$\eta \cdot 10^3$	$\Delta\eta, \%$	$\eta \cdot 10^3$	$\Delta\eta, \%$	$\eta \cdot 10^3$	$\Delta\eta, \%$		
0.00	7.240	-0.10	6.423	+0.63	5.716	-0.14	2197.0	$\bar{6}.93338$
6.40	7.097	+2.09	6.251	+2.04	5.559	+0.54	2260.6	$\bar{6}.88641$
12.15	6.870	+1.34	6.034	+1.61	5.354	+0.33	2319.8	$\bar{6}.83797$
22.95	6.699	+0.23	5.834	+0.81	5.137	+0.26	2436.7	$\bar{6}.75712$
32.79	6.673	+0.07	5.795	+0.48	5.102	-0.25	2550.5	$\bar{6}.69244$
39.12	6.724	+0.33	5.817	+0.19	5.086	-0.33	2625.3	$\bar{6}.65371$
47.26	6.865	-0.12	5.865	-0.51	5.153	-0.15	2726.3	$\bar{6}.60672$
59.89	7.239	-0.17	6.192	+0.23	5.339	-0.39	2891.2	$\bar{6}.54081$
75.20	7.883	-0.31	6.679	+0.12	5.694	-0.51	3104.5	$\bar{6}.46804$
88.19	8.644	-0.02	7.360	-0.23	6.227	-0.84	3295.8	$\bar{6}.44623$
100.00	9.849	+0.07	8.187	+0.27	6.881	-0.58	3480.8	$\bar{6}.38680$

TABLE 3

The System Propyl Alcohol - Dichloroethane

C ₃ H ₇ OH (in moles %)	Viscosity, calculated according to Panchenkov's formula						E ₁₂ = 2771.0	
	30°		40°		50°		E _c	log A _s
	$\eta \cdot 10^3$	$\Delta\eta, \%$	$\eta \cdot 10^3$	$\Delta\eta, \%$	$\eta \cdot 10^3$	$\Delta\eta, \%$		
0.00	7.249	-0.10	6.423	+0.63	5.716	-0.14	2197.0	$\bar{6}.93338$
11.82	7.049	+1.14	6.175	+1.41	5.469	-0.25	2347.8	$\bar{6}.83115$
21.63	7.153	+3.84	6.237	+1.23	5.461	-0.49	2496.3	$\bar{6}.74809$
32.60	7.392	+1.77	6.385	+1.46	5.566	+0.43	2687.7	$\bar{6}.63714$
55.79	8.984	-0.26	7.578	+0.20	6.465	-0.29	3176.3	$\bar{6}.42860$
67.20	10.324	-0.15	8.579	+0.76	7.195	-0.21	3460.2	$\bar{6}.31234$
83.60	13.226	-0.41	10.737	+0.24	8.857	-0.17	3917.5	$\bar{6}.13535$
100.00	17.685	+0.03	14.015	+1.13	11.277	-0.02	4433.5	$\bar{7}.94092$

2. A "bond energy - composition" diagram was constructed. The presence of a maximum on the "bond energy-composition" curve is evidence of chemical reaction of the components. "Bond energy - composition" curves which were convex toward the abscissa axis indicate the absence of reaction of the components.

TABLE 4

The System n-Butyl Alcohol—Dichloroethane

C ₄ H ₉ OH (in moles %)	Viscosity, calculated according to Panchenkov's formula						E ₁₂ = 3030.8	
	30°		40°		50°		E _c	log A _s
	$\eta \cdot 10^3$	$\Delta\eta\%$	$\eta \cdot 10^3$	$\Delta\eta\%$	$\eta \cdot 10^3$	$\Delta\eta\%$		
0.00	7.249	-0.10	6.423	+0.63	5.716	-0.14	2197.0	6.93338
9.69	7.255	+1.60	6.331	+2.13	5.600	+0.29	2366.3	6.82761
20.52	7.507	+0.78	6.521	+1.50	5.707	-0.05	2569.3	6.72109
31.78	8.150	+0.85	7.014	+1.36	6.074	+0.21	2809.8	6.60610
46.83	9.409	-0.10	7.955	+0.80	6.743	-0.71	3157.8	6.45067
56.18	10.568	-0.46	8.824	+1.03	7.449	+0.03	3392.7	6.35333
67.68	12.900	+0.66	10.522	+1.56	8.784	+0.84	3701.9	6.24085
85.60	17.408	-0.18	13.935	+1.09	11.325	+0.86	4225.5	6.04099
100.00	22.586	+0.17	17.634	+0.26	13.987	-0.45	4685.0	7.86885

TABLE 5

The system Isoamyl Alcohol—Dichloroethane

iso-C ₅ H ₁₁ OH (in moles %)	Viscosity, calculated according to Panchenkov's formula						E ₁₂ = 3021.0	
	30°		40°		50°		E _c	log A _s
	$\eta \cdot 10^3$	$\Delta\eta\%$	$\eta \cdot 10^3$	$\Delta\eta\%$	$\eta \cdot 10^3$	$\Delta\eta\%$		
0.00	7.249	-0.10	6.423	+0.63	5.716	-0.14	2197.0	6.93338
12.72	7.510	+1.07	6.578	+1.57	5.825	+0.67	2453.5	6.79261
22.01	7.954	-0.20	6.903	+0.55	6.034	+0.07	2640.1	5.70503
32.69	9.150	+1.06	7.819	+2.22	6.749	+1.48	2913.1	6.59189
43.02	10.275	-0.11	8.669	+1.04	7.384	+0.26	3213.3	6.45055
57.65	13.000	+0.12	10.704	+0.53	8.923	+0.06	3699.2	6.23624
66.39	15.435	+0.74	12.492	+1.58	10.242	+0.96	4023.0	6.09717
80.49	20.960	+0.73	16.417	+1.39	13.082	-0.07	4599.2	7.84506
88.80	25.046	-0.21	19.288	+0.99	15.083	+0.07	4969.8	7.67478
100.00	32.665	-0.02	24.465	+0.71	18.650	-0.08	5505.5	7.42849

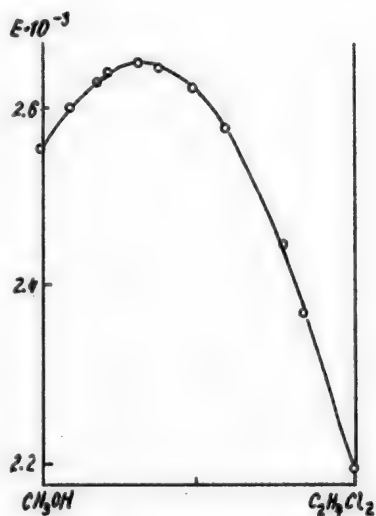


Fig. 1. Dependence of the bond energy of the molecules on the composition in the system methyl alcohol-dichloroethane.

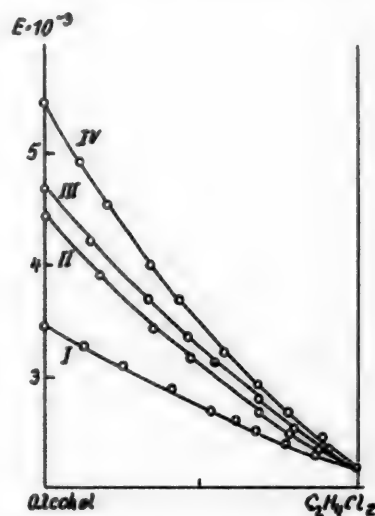


Fig. 2. "Bond energy - composition" curves of the systems: I) Ethyl alcohol - dichloroethane; II) propyl alcohol - dichloroethane; III) butyl alcohol - dichloroethane; IV) isoamyl alcohol - dichloroethane.

LITERATURE CITED

- [1]. G. M. Panchenkov. Theory of Viscosity of Liquids. State Fuel, Tech. Press (1947).
- [2]. G. M. Panchenkov, J. Phys. Chem., 24, 1930 (1950).
- [3]. G. M. Panchenkov, Proc. Acad. Sci. USSR. 79, 6, 985 (1951).
- [4]. V. V. Udovenko, R. P. Alrapetova and R. I. Filatova, J. Gen. Chem., 21, 1430 (1951).*

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INVESTIGATION IN THE FIELD OF CONJUGATED SYSTEMS

LIV. THE ORDER OF ADDITION OF HYPOBROMOUS ACID TO VINYLALKYLACETYLENES. SYNTHESIS AND PROPERTIES OF α -OXIDES OF VINYLACETYLENES

A. A. Petrov

It was shown in the preceding articles that bromine [1] and alkylhypohalogenites [2] add to vinylalkylacetylenes at the double bond. The triple bond practically does not enter into the reaction and 1,4-addition does not occur. The substances obtained were used for the synthesis of enyne halogen derivatives, acetylenic ketones and their enolic ethers.

It can be assumed that the same order of addition will be observed in the addition to vinylalkylacetylenes of hypohalogen acids. With the object of establishing the order of addition of hypobromous acid to vinylalkylacetylenes we investigated the reaction of vinylmethyl- and vinylethylacetylene with an aqueous solution of bromoacetamide [3].

Vinylalkylacetylenes can add HOBr with the formation of six substances: three of these are alcohols and three ketones.



The addition products of HOBr actually obtained boiled in a narrow temperature range and had the following chemical properties.

1. They yielded acetates as a result of the action of acetic anhydride. Thus, they consisted of alcohols and not of ketones and, consequently, formulas (III), (IV) and (VI) are excluded.

2. Upon distillation over KOH they yielded α -oxides of vinylalkylacetylenes. This conversion forces us to reject all the possible formulas for the bromohydrins except (I) and (II). The second formula was very slightly probable, since such an order of addition has never been observed for HOBr. A bromohydrin with a formula similar to (II) was obtained by the addition of hydrogen bromide to the α -oxide of vinylmethylacetylene. It was markedly different from the addition product of HOBr to vinylmethylacetylene in its index of refraction.

Thus, it was established that hypobromous acid adds to vinylalkylacetylene at the double bond with formation of the bromohydrins (I).






This experimental fact is of interest from two points of view. In the first place, it is once more evidence of the presence of displacement of electrons in the molecules of vinylalkylacetylenes under the influence of alkyl radicals toward the double bond which consequently becomes more reactive. In the second place, it discloses the route to the simple preparation of acetylenic oxides which have hitherto been hard-to-obtain substances.

Only the first representative of the homologous series of acetylenic oxides of this type with normal structure was known [4]. We have prepared the next two homologs.

The constants of a number of previously known acetylenic oxides which were described in the present work are presented in the table.

It is evident from the table that the character of substitution in this oxide series markedly influences the constants. Oxides with a normal carbon atom chain have a considerably higher boiling point in comparison with isomers with a branched structure and with their normal saturated analogs (the oxide $CH_2=CH-CH_2-CH_2-CH_3$ boils

at 58.5-59° [7], the oxide $CH_2=CH-CH_2-CH_2-CH_2-CH_3$ at 123-124° [8]). They also differ in the considerably greater indexes of refraction and specific gravities. The values of the molecular refraction found for them exceed the calculated values to a greater extent than in the case of unsubstituted oxides and oxides with a branched structure.

Substance	Boiling point	d_4^{20}	n_D^{20}	MR _D	
				Found	Calculated
 $\text{CH}_2\text{-CH-C}\equiv\text{CH}$ [4]	86-87°	0.945 (23°)	1.427	18.50	18.11
 $\text{CH}_2\text{-CH-C}\equiv\text{C-CH}_3$	125.5-126.5	0.9499	1.4542	23.41	22.73
 $\text{CH}_2\text{-C(CH}_3\text{)-C}\equiv\text{CH}$ [5]	91-91.5	0.8939 (18°)	1.4205	23.27	22.73
 $\text{CH}_2\text{-CH-C}\equiv\text{C-CH}_2\text{-CH}_3$	142-143	0.9182	1.4530	28.30	27.35
 $\text{CH}_2\text{-C(CH}_3\text{)}_2\text{-C}\equiv\text{C-CH}_3$ [6]	40-41 (22 mm)	0.9264 (9°)	1.4461	27.70	27.60

Of the chemical properties of the oxides obtained by us we investigated the addition of water, methyl alcohol and hydrogen bromide to methylacetylenylethyleneoxide.

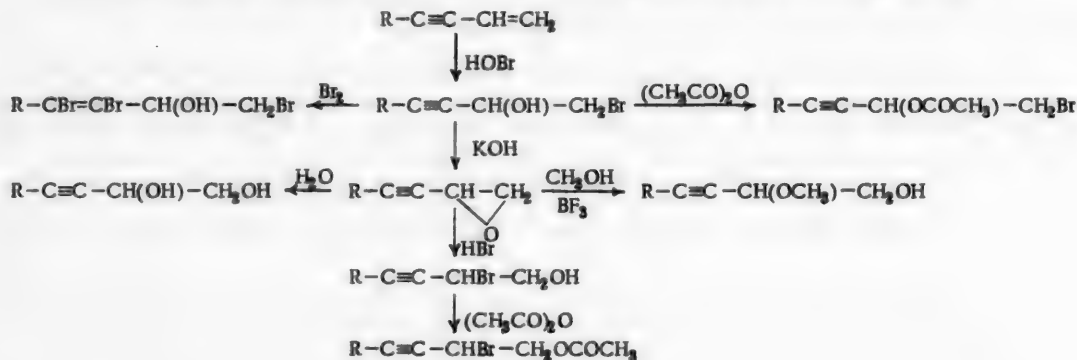
The addition of water proceeds very readily - upon heating for 3 hours to 100°.

According to the literature data acetylenylethylene oxide requires heating at that same temperature for 20 hours for conversion into the glycol [4]. The glycol thereby formed is a crystalline substance with a higher melting point (56-57°) than that of the unsubstituted glycol (39.5-40.5°) [4].

In exactly the same way the reaction of the oxide under investigation with methyl alcohol in the presence of the etherate of boron fluoride proceeds very readily. In accordance with the previously established rule of addition of alcohols to unsaturated oxides in the presence of BF_3 [9], which was confirmed for acetylenic oxides by Perveev [10], the glycol ether obtained was assigned the structure of a primary alcohol.

As a result of the addition to the same oxide of hydrogen bromide, a bromohydrin was obtained which was isomeric with that formed by the action of HOBr on vinyl-methylacetylene [11]. In comparison with the latter it was considerably more readily acetylated, which was an extra indication of the primary character of the hydroxyl group.

The conversions described in the present article are presented in the following scheme:



EXPERIMENTAL

1. Preparation and Properties of the Bromohydrins

Vinylmethylacetylene (90 g, a double excess) was shaken for a duration of 30 minutes with bromoacetamide acidified with H_2SO_4 which contained 0.72 moles of this substance in 1 liter. The bromoacetamide solution was preliminarily cooled until considerable quantities of ice formed.

The bromohydrin was extracted with ether from the aqueous solution (after its filtration through cotton and saturation with sodium chloride). The bromohydrin was extracted from the oil (after distilling off the excess hydrocarbon and concentrating to a small volume) initially with water and then from the water with ether. The quantity of insoluble products (bromides, probably) proved to be negligible (4 g). About 6.5 g of the bromohydrin dissolved in 100 ml of water.

Upon vacuum distillation the substance almost entirely passed over at a constant temperature. The yield of pure substance amounted to about 82 g (70%). The residue from the distillation was 6 g (a resinified mass).

B. p. 89.5° at 10 mm, 103-103.5° at 20 mm; d_4^{20} 1.5124; n_D^{20} 1.5172; MR_D 32.62. C_8H_7OBr . Calculated 32.48.

0.1420 g sub.: 0.1634 g AgBr. 0.1348 g sub.; 13.28 g benzene: Δt 0.315°. Found %: Br 48.97. M 163.2. C_8H_7OBr . Calculated %: Br 49.03. M 163.0.

The bromohydrin of vinyl ethylacetylene was obtained in a yield of 40% by the same method.

B. p. 96.5-97° at 10 mm; 108-108.5° at 20 mm; d_4^{20} 1.4071; n_D^{20} 1.5070; MR_D 37.45. C_6H_9OBr . Calculated 37.20.

0.1268 g sub.: 0.1346 g AgBr. Found %: Br 45.17. C_6H_9OBr . Calculated %: Br 45.14.

Both bromohydrins were converted into the acetates (yield 85%) by the action of a 50% excess of acetic anhydride and 1 drop of H_2SO_4 .

The following constants were found for the acetate of the bromohydrin of vinylmethylacetylene:

B. p. 98° at 10 mm; 112.5-113° at 20 mm; d_4^{20} 1.3970; n_D^{20} 1.4864; MR_D 42.17. $C_7H_9O_2Br$. Calculated 41.84.

0.1656 g sub.: 0.1527 g AgBr. Found %: Br 39.24. $C_7H_9O_2Br$. Calculated %: Br 39.06.

The following constants were found for the acetate of the bromohydrin of vinyl ethylacetylene:

B.p. 104.5-105° at 10 mm; d_4^{20} 1.3267; n_D^{20} 1.4820; MR_D 47.08. $C_8H_{11}O_2Br$. Calculated 46.56.

0.1428 g sub.: 0.1238 g AgBr. Found %: Br 36.89. $C_8H_{11}O_2Br$. Calculated %: Br 36.48.

1,3,4-Tribromopenten-3-ol-2 was obtained in a yield of 88% by the action of the calculated quantity of bromine in chloroform on the bromohydrin of vinylmethylacetylene.

B.p. 135.5° at 8 mm; 139.5° at 10 mm; d_4^{20} 2.2090; n_D^{20} 1.5918; MR_D 49.44. $C_6H_7OBr_3$. Calculated 50.31.

0.1744 g sub.: 0.3046 g AgBr. Found %: Br 74.32. $C_6H_7OBr_3$. Calculated %: Br 74.26.

2. Preparation and Properties of the Oxides of Vinylalkylacetylenes

The oxides of vinylalkylacetylenes were prepared by distilling the bromohydrins or their acetates over concentrated KOH. The substances were introduced in the form of drops into the heated alkali while the distillate was being continuously distilled off. The yield of oxides amounted to around 85%. The constants are given in the table.

The following constants were found for the oxide of vinylmethylacetylene:

0.1663 g sub.: 0.4467 g CO_2 ; 0.1163 g H_2O . Found %: C 73.30; H 7.86; C_5H_6O . Calculated %: C 73.14; H 7.37.

The following constants were found for the oxide of vinyl ethylacetylene:

0.1810 g sub.: 0.4956 g CO_2 ; 0.1365 g H_2O . Found %: C 74.72; H 8.44. C_6H_8O . Calculated %: C 74.96; H 8.39.

The glycol was obtained by heating the oxide of vinylmethylacetylene with a 5-fold quantity of water in a sealed glass tube at 100° for 3 hours. The latter was separated from water by salting it out with potash, was dissolved in ether, and the ethereal solution was dried with roasted potash. The yield of glycol amounted to 60%.

M.p. 56-57° (from benzene) b.p. 111.5-112.5° at 8 mm.

0.1606 g sub.: 0.3531 g CO_2 ; 0.1163 g H_2O . Found %: C 60.01; H 8.10. $C_5H_8O_2$. Calculated %: C 59.98; H 8.06

The glycol consisted of colorless crystals, quite soluble in alcohol and ether, more poorly soluble in chloroform and difficultly soluble in cold benzene.

Evolution of heat was observed during the action on a solution of 6 g of the oxide in 50 ml of methyl alcohol of 1 drop of the etherate of boron fluoride. After standing for 5 hours the liquid was neutralized with solid KOH and subjected to distillation, initially at ordinary pressure and then in a vacuum. The yield of the monoether of the glycol amounted to 6 g (72%).

B.p. 72.5° at 10 mm; 84-84.5° at 20 mm; d_4^{20} 0.9925; n_D^{20} 1.4572; MR_D 31.33. $C_6H_{10}O_2$ \bar{F} . Calculated 31.07.

0.1623 g sub.: 0.3773 g CO_2 ; 0.1307 g H_2O . 0.0778 g sub.: 0.1606 g AgI (according to Zeisel's method). Found %: C 63.44; H 9.01; OCH_3 27.28. $C_6H_{10}O_2$. Calculated %: C 63.13; H 8.83; OCH_3 27.13.

By the careful addition of the oxide to concentrated hydrobromic acid a bromohydrin was obtained in a yield of about 70% which was isomeric with that obtained from the hydrocarbon.

B.p. 88.5-89° at 10 mm; 102-103° at 20 mm; d_4^{20} 1.5120; n_D^{20} 1.5312; MR_D 33.37. C_6H_7OBr . Calculated 32.46.

0.1418 g sub.: 0.1641 g AgBr. Found %: Br 49.25. C_6H_7OBr . Calculated %: Br 49.03.

When a solution of this bromohydrin in acetic anhydride was let stand, a reaction, notable for the evolution of heat, began without the addition of acid.

The acetate of this bromohydrin had the following properties:

B.p. 97-97.5° at 10 mm; 111.5-112° at 20 mm; d_4^{20} 1.3956; n_D^{20} 1.4938; MR_D 42.76. $C_7H_9O_2Br$ \bar{F} . Calculated 41.84.

0.1610 g sub.: 0.1484 g AgBr. Found %: Br 39.22. $C_7H_9O_2Br$. Calculated %: Br 39.06.

The oxide of vinylmethylacetylene, described above, was obtained by distilling this bromohydrin or its acetate over KOH.

SUMMARY

1. The order of addition of hypobromous acid to vinylmethyl- and vinyl-ethyl-acetylenes was investigated. It was established that the addition proceeds at the ethylenic bond. The corresponding bromohydrins, their acetates and the bromide were isolated and characterized.

2. The oxides of vinylmethyl- and vinyl-ethylacetylenes were obtained for the first time by the action of caustic alkali on the bromohydrins. The hydration of the first oxide and the addition of methyl alcohol and of hydrogen bromide were investigated.

LITERATURE CITED

- [1] A. A. Petrov and Yu. I. Profiryeva, Proc. Acad. Sci. USSR, 89, 873 (1953); J. Gen. Chem., 23, 1867 (1953)*
- [2] A. A. Petrov and Yu. I. Profiryeva, Proc. Acad. Sci. USSR, 90, 561.
- [3] A. A. Petrov, J. Gen. Chem., 8, 142 (1938).
- [4] M. Lespieau, Comptes rend., 180, 442 (1925).
- [5] N. A. Gershtein, J. Gen. Chem., 12, 132 (1942).
- [6] F. Ya. Perveev, J. Gen. Chem., 19, 1303 (1949).**
- [7] M. de Montmolin, P. Matile, Helv. Chem. Acta, 7, 106 (1923).
- [8] B. Rothstein, Bull. Soc. Chim., (5), 2, 1936 (1935).
- [9] A. A. Petrov, Proc. Acad. Sci. USSR, 50, 249 (1945); J. Gen. Chem., 16, 1625 (1946).
- [10] F. Ya. Perveev and N. I. Kudryasheva, J. Gen. Chem., 22, 1580, 1964 (1952)***; 23, 1673 (1953)****.
- [11] A. A. Petrov, J. Gen. Chem., 11, 991 (1941); 10, 1418 (1940).

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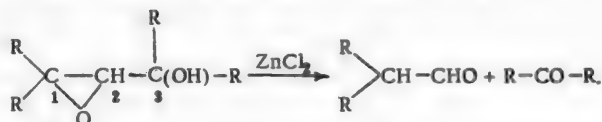
INVESTIGATIONS IN THE FIELD OF ALCOHOL OXIDES (OXIDOLS)

IV. PROPERTIES OF THE α -OXIDES OF ALLYL AND PROPENYL DERIVATIVES OF PHENOL AND o-CRESOL

V. I. Pansevich-Kolyada and Z. B. Idelchik

The unique properties of α,β -alcohol oxides, which are doubtless due to the presence in their structure of two functional groups bound to neighboring carbon atoms, were established by the preceding investigations [1,2,3] of these compounds. It was also shown that the behavior of the oxide ring of these substances in chemical reactions is to a considerable extent dependent on the radicals adjacent to the oxide carbon atoms.

A general property of all the oxidols investigated by us appears to be their acetylation at the hydroxyl group upon heating with acetic anhydride and the formation of oxidoacetates due to the preservation of the oxide ring. A certain difference between the oxidols of the aliphatic series and those with aromatic radicals is observed in the reaction with anhydrous zinc chloride. Upon heating with fused zinc chloride, oxidols of the fatty series are cleaved at the bond between carbon atoms 2 and 3 with formation of aldehydes and ketones:



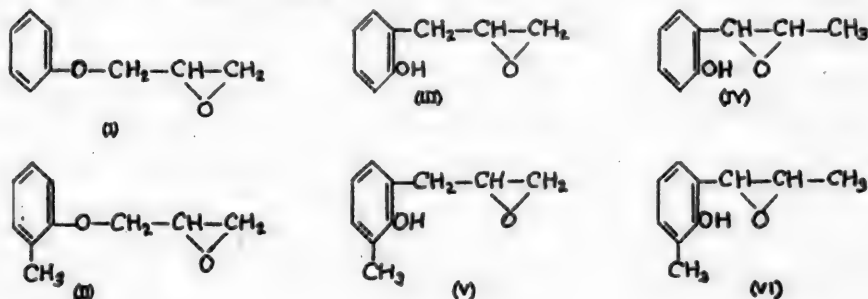
An oxidol with a phenyl radical at the tertiary alcoholic group, 2-methyl-4-phenyloxido-2,3-pentanol-4 [1] proves to be very unstable and is cleaved into acetophenone and isobutyraldehyde upon being kept in a desiccator over H_2SO_4 , P_2O_5 , or CaCl_2 at room temperature. The oxidol 2-methyl-4-benzyloxido-2,3-pentanol-4 [3], in which the phenyl radical is separated from the tertiary alcoholic group by a CH_2 group, is isomerized into the unsaturated glycol 2-methyl-4-benzylpenten-2-diyl-3,4 by the action of zinc chloride and dilute sulfuric acid, while on heating with an aqueous solution of ammonia it yielded the aminodiol 2-methyl-4-benzyl-3-aminopentadiol-2,4.

It was established that 2-methyl-4-benzyloxido-2,3-pentanol-4 and the unsaturated glycol are capable of mutual interconversion which proceeds with disruption and reduction of the oxide ring. These conversions appear to be a hitherto unobserved form of tautomerism which we call oxidoenolic tautomerism.

In the present work the study of α -oxides of allyl and propenyl derivatives of phenol and o-cresol is carried out; it turned out in the course of this work that the properties of the oxide ring of these compounds are no less interesting and unique than those of the previously studied oxidols, and are determined to a considerable extent by the distance of the oxide ring from the benzene ring.

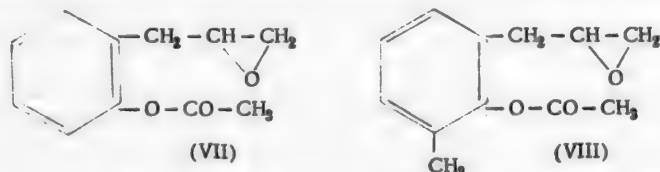
We synthesized the allyl ethers of phenol and o-cresol by the Claisen reaction [4,9]; o-allylphenol and o-allyl-o-cresol were obtained via the rearrangement of these ethers. o-Propenylphenol and o-propenyl-o-cresol were obtained by the isomerization of o-allylphenol and o-allyl-o-cresol.

The allyl and propenyl derivatives of phenol and o-cresol were oxidized by peroxyacetic acid and for all, except the allyl ether of o-cresol, the corresponding oxides were obtained:



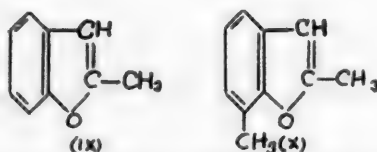
The oxide of the allyl ether of o-cresol (II) proved to be a very unstable compound and on vacuum distillation was almost entirely split with recovery of o-cresol, while only an insignificant portion of the substance had data close to those calculated for the oxide of the allyl ether of o-cresol.

Upon boiling the oxides of o-allylphenol (III) and o-allyl-o-cresol (V) with acetic anhydride, acetylation, similar to that previously studied for alcohol oxides [2,3], proceeded at the phenolic hydroxyl group with retention of the oxide ring; the oxidoacetates (VII) and (VIII) were thereby obtained:

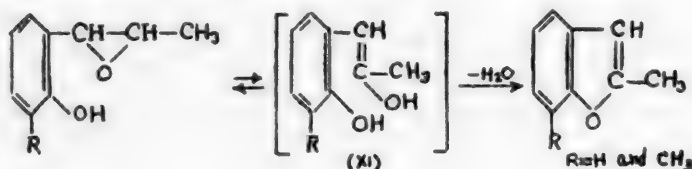


α -Oxides are isomerized under the action of zinc chloride, as is well known [5], depending on the location of the oxide ring in the aldehyde or ketone. The behavior toward this reagent of α, β -alcohol oxides is identical, as indicated above, and depends on the radicals adjacent to the oxide carbon atoms. In contrast to these substances, the oxide of o-allylphenol (III) remains unchanged on heating with anhydrous zinc chloride.

The oxides of o-propenylphenol (IV) and o-propenyl-o-cresol (VI) are quite different from all the oxidols previously studied by us. These substances are not appreciably changed in air; however when kept in a desiccator over sulfuric acid at room temperature the formation of cumarone derivatives occurred, respectively: 2-methylcumarone (IX) and 2,7-dimethylcumarone (X):



The formation of cumarone derivatives from the oxidophenols (IV) and (VI) is possible only via the preliminary conversion of the oxidophenols into the unsaturated phenolalcohols (XI) which, eliminate a molecule of water similar to the 1,4-glycols [7], and yield cumarone derivatives:



On boiling the oxide of o-propenyl-o-cresol (VI) with acetic anhydride, dehydration and formation of 2,7-dimethylcumarone (X) also occurred. It is necessary to assume that the behavior of the oxide of o-propenylphenol (IV) with acetic anhydride will be the same, but on account of the absence of the substance we cannot establish this.

The conversion of the oxidophenols (IV) and (VI) into the cumarone derivatives (IX) and (X) can be explained by the presence of oxidoenolic tautomerism [3] and in its turn serves to confirm it.

The oxides of o-propenylphenol (IV) and o-propenyl-o-cresol (VI) are in equilibrium with their enolic form (XI). When they are kept in air, the equilibrium is displaced toward the oxido form. In the presence of dehydrating substances the equilibrium is displaced toward the enol form due to the consumption of the enol in the formation of a furan ring. The readiness with which the furan ring is formed is explained by the 1,4-position of the enolic hydroxyl groups which are close together when the double bonds are formed.

The quantity of hydroxyl groups, determined by Tserevitinov's method in the oxide of o-propenyl-o-cresol, which is a liquid substance, was found to be 1.14 % greater than the calculated value, which also serves as a confirmation of the presence of the enol form together with the oxide.

Thus, the properties of the α -oxides of allyl and propenyl derivatives of phenols are identical and also differ from the properties of α, β -alcohol oxides. In allylphenol oxides the oxide ring is passive and remains unchanged by

the action not only of acetic anhydride, but also of zinc chloride. The oxide ring of the oxides of the o-propenylphenols is very stable due to the presence in it of the phenyl radical and the oxides of o-propenylphenols are capable of being converted into their unsaturated tautomeric enols with a hydroxyl group at the double bond. Under suitable conditions the enols formed readily eliminate a molecule of water, due to the hydroxyl groups of the enol and phenol and yield cumarone derivatives.

EXPERIMENTAL

Oxidation of the Allyl Ether of Phenol with Peroxyacetic Acid

The allyl ether of phenol was prepared by heating a mixture of phenol with allyl bromide and anhydrous potash in acetone [4].

B.p. 82° (10 mm); n_D^{20} 1.5193; d_4^{20} 0.9796; MR_D 41.54; Calculated 41.35.

15.5 g of 73% peroxyacetic acid was slowly added to 20 g of allyl ether in 40 ml of dry ether. The oxidation proceeded slowly without evolution of heat or change in the color of the reaction mixture. After 22 days all the peroxyacetic acid had reacted and consequently the acetic acid was neutralized with soda, the reaction products were extracted with ether, dried with $MgSO_4$ and vacuum distilled. 6 g of substance (I) with a b.p. of 101-105° (4.5 mm) was isolated. This was a mobile yellow colored liquid with the odor of tobacco.

n_D^{20} 1.5311; d_4^{20} 1.1145; MR_D 41.63; Calculated 40.68.

0.2456 g sub.: 0.6453 g CO_2 ; 0.1513 g H_2O . 0.1496, 0.2889 g sub.: 21.08 g benzene: Δt 0.254, 0.462°. Found %: C 72.10; H 6.89; M 143.4, 147.7. $C_9H_{10}O_2$. Calculated %: C 72.0; H 6.66; M 150. It contained no active hydrogen.

Oxidation of o-Allylphenol with Peroxyacetic Acid

o-Allylphenol was prepared by boiling the allyl ether of phenol in a stream of carbon dioxide [4].

B.p. 97-98° (8 mm); n_D^{20} 1.5440; d_4^{20} 1.0210; MR_D 41.48; calculated 41.22. Found %: OH 12.27. Calculated %: OH 12.68.

26 g of 93% peroxyacetic acid was slowly added to 42 g of o-allylphenol in 84 ml of dry ether. The oxidation proceeded with evolution of heat; the temperature of the mixture was maintained at 20-25°. The color of the reacting substances became orange. After 3 days the peroxyacetic acid had reacted. The oxidation products were treated, as indicated above, dried with $MgSO_4$ and vacuum distilled. 19.3 g of substance (III) with a b.p. of 154° (15 mm) was obtained. It was a mobile, odorless, light orange liquid which contained active hydrogen.

n_D^{20} 1.5558; d_4^{20} 1.1795; MR_D 40.88; calculated 40.56.

0.2245 g sub.: 0.5892 g CO_2 ; 0.1358 g H_2O . 0.2473 g sub.: 37.92 ml CH_4 (0°, 760 mm). 0.1486 g sub.: 16.11 g benzene; Δt 0.312°. Found %: C 71.6; H 6.83; OH 11.71; M 151.9. $C_9H_{10}O_2$. Calculated %: C 72.00; H 6.66; OH 11.33; M 150.

Reaction of the Oxide of o-Allylphenol with Acetic Anhydride

2 g of the oxide was boiled for 4 hours with 10 g of acetic anhydride. The acetic anhydride was eliminated and the reaction products were vacuum distilled. 1.5 g of a colorless mobile liquid (VII) with a sharp odor was isolated.

B.p. 142-143° (8 mm); n_D^{20} 1.5220; d_4^{20} 1.1550; MR_D 50.71; calculated 49.92.

0.1988 g sub.: 0.5003 g CO_2 ; 0.1128 g H_2O . 0.0965, 0.2124 g sub.: 17.19 g benzene. Δt 0.159, 0.352°. Found %: C 68.63; H 6.3; M 181.5; 180.42. $C_{11}H_{12}O_3$. Calculated %: C 68.75; H 6.25; M 192. (Active hydrogen was absent).

The Action of Zinc Chloride on the Oxide of o-Allylphenol

1.5 g of finely divided anhydrous zinc chloride was added to 5.5 g of oxidophenol in 25 ml of dry ether and the mixture was heated for 1.5 hours on a boiling water bath. After eliminating the ether the substance was vacuum distilled. 3 g of substance was obtained; the carbonyl group was absent.

B.p. 133.5° (7 mm); n_D^{20} 1.5580; d_4^{20} 1.1780; MR_D 40.37; calculated 40.56.

The oxide of o-allylphenol was recovered without change.

Oxidation of o-Propenylphenol with Peroxyacetic Acid

o-Propenylphenol was prepared by isomerizing o-allylphenol [6].

B.p. 154° (21 mm); m.p. 33-34°. Found %: C 80.78; H 7.68. Calculated %: C 80.6; H 7.49.

17.8 g of 73% peroxyacetic acid was slowly added to 23 g of *o*-propenylphenol, dissolved in 46 ml of dry ether. The oxidation proceeded with evolution of heat; the temperature was maintained at 20-25°. The contents of the flask acquired an orange color toward the end of the oxidation. After two days there was no peroxide present. The products of the reaction were treated, as indicated above, with dried MgSO_4 and, after distilling off the ether, were vacuum distilled. 15 g of a substance was obtained which boiled at 147-148° (10 mm). After some time the substance crystallized as white needles, readily soluble in ether, alcohol, chloroform, and benzene, and poorly soluble in petroleum ether. They were recrystallized from the latter and 14 g of coarse flakes with a m.p. of 58-59° was obtained. The substance (IV) contained active hydrogen.

0.1158 g sub.: 0.3054 g CO_2 ; 0.0696 g H_2O . 0.0893 g sub.: 15.02 ml CH_4 (22°, 746 mm). 0.1479 g sub.; 17.89 g benzene: Δt 0.273°. Found %: C 71.92; H 6.75; OH 11.32; M 155.6. $\text{C}_9\text{H}_{10}\text{O}_2$. Calculated %: C 72.0; H 6.66; OH 11.3; M 150.

Upon keeping this crystalline substance in a desiccator over sulfuric acid overnight an oily, dirty-yellow colored liquid with the odor of toluene was formed. By fractionally distilling the liquid, substance (IX) with a b.p. of 76-77° (8 mm) was formed which did not contain active hydrogen.

n_D^{20} 1.5580; d_4^{20} 1.0581; MR_D 39.31; calculated 39.34.

0.1540 g sub.: 0.4635 g CO_2 ; 0.0844 g H_2O . 0.0894, 0.1955 g sub.: 1974 g benzene: Δt 0.186, 0.399°. Found %: C 82.08; H 6.13; M 125.2, 127.8. $\text{C}_9\text{H}_8\text{O}$. Calculated %: C 81.80; H 6.60; M 132.

From the substance with b.p. 76-77° (8 mm) a picrate was formed which melted at 74-79° and was cleaved in a desiccator over sulfuric acid into picric acid and methylcumarone; this is in agreement with the literature data for methylcumarone picrate [8].

Oxidation of the Allyl Ether of *o*-Cresol with Peroxyacetic Acid

The allyl ether of *o*-cresol was prepared by the method described for the preparation of the allyl ether of phenol [4, 9]. It boiled at 76-77° (4 mm).

n_D^{20} 1.5190; d_4^{20} 0.9658; MR_D 46.47; calculated 45.95. No active hydrogen was contained in the substance.

15.6 g of 65% peroxyacetic acid was added to 20 g of the allyl ether of *o*-cresol in 40 ml of anhydrous ether. No evolution of heat occurred; however the reaction mixture acquired a straw-yellow color. After 22 days no peroxide was present in the mixture. The reaction products were treated analogously to those in the preceding experiments.

Upon fractional distillation of the oxidation products at 8.5 mm, the bulk distilled over at 82-84°. This proved to be *o*-cresol. The arylglycolic acid obtained from it had a m.p. of 154°. A mixed sample with a preparation obtained by a known method gave no melting point depression. Only a total of 0.5 g of a substance with a b.p. of 129-131° (8.5 mm) was obtained; it was apparently the oxide of the allyl ether of *o*-cresol (II).

n_D^{20} 1.5270; d_4^{20} 1.0905; MR_D 46.24; calculated 45.29.

0.1900 g sub.: 0.5011 g CO_2 ; 0.1267 g H_2O . 0.1173 g sub.: 21.21 g benzene: Δt 0.182°. Found %: C 71.93; H 7.46; M 156.7. $\text{C}_{10}\text{H}_{12}\text{O}_2$. Calculated %: C 73.10; H 7.30; M 164.

The substance contained an insignificant admixture which contained active hydrogen; this was reflected in the analytical results.

Oxidation of *o*-Allyl-*o*-cresol with Peroxyacetic Acid

The *o*-allyl-*o*-cresol was prepared analogously to the *o*-allylphenol [4].

B.p. 92-94° (6 mm); n_D^{20} 1.5377; d_4^{20} 1.0010; MR_D 46.22; calculated 46.83.

15.6 g of 93% peroxyacetic acid was added to 28 g of the substance in 56 ml of dry ether. The oxidation proceeded smoothly, the temperature increased slowly and the color of the mixture became bright orange. After 3 days the oxidation was completed. The reaction products were treated analogously to those of the preceding experiments and vacuum distilled. 8 g of substance (V) with a bright orange color was obtained.

B.p. 146° (10 mm); n_D^{20} 1.5468; d_4^{20} 1.1213; MR_D 46.37; calculated 45.18.

0.2564 g sub.: 0.6910 g CO_2 ; 0.1710 g H_2O . 0.1208 g sub.: 15.92 ml CH_4 (0°, 760 mm). 0.1005, 0.2358 g sub.; 16.47 g benzene: Δt 0.175, 0.425°. Found %: C 73.50; H 7.46; OH 10.07; M 175.7, 177.4. $\text{C}_{10}\text{H}_{12}\text{O}_2$. Calculated %: C 73.17; H 7.32; OH 10.3; M 164.

Reaction of the Oxide of o-Allyl-o-cresol with Acetic Anhydride

10 g of acetic anhydride was added to 2 g of the substance and the mixture was boiled for 5 hours in a flask equipped with a reflux condenser. The acetic anhydride was distilled off in a vacuum and 1.2 g of substance (VIII) was obtained by fractional distillation of the reaction products.

B.p. 128-129° (2 mm); n_D^{20} 1.5045; d_4^{20} 1.1230; MR_D 54.35; calculated 54.54.

0.2050, 0.1483 g sub.: 0.5044, 0.3677 g CO_2 ; 0.1277, 0.0955 g H_2O . 0.1192, 0.2206 g sub.: 15.3 g benzene; Δt 0.223, 0.415°. Found %: C 67.10, 67.62; H 6.96, 7.20; M 179.2, 178.6. $C_{12}H_{14}O_3$. Calculated %: C 69.9; H 6.79; M 206. The test for active hydrogen was negative.

A repeated experiment involving the preparation of the acetyl derivative did not give better analytical results. Apparently, the reaction products are partially changed during the distillation.

Oxidation of o-Propenyl-o-cresol with Peroxyacetic Acid

o-Propenyl-o-cresol was prepared analogously to o-propenylphenol. It boiled at 125-127° (10 mm). It partially crystallized on standing. 35 g of o-propenyl-o-cresol was dissolved in 80 ml of anhydrous ether and oxidized with 24 g of 73% peroxyacetic acid. The reaction proceeded very energetically with marked evolution of heat. After 3 days there proved to be no peroxide in the mixture. The reaction products were treated as indicated for the preceding cases, and after drying with $MgSO_4$, were distilled. 10 g of an orange colored oily substance (VI) with the odor of phenol was obtained.

B.p. 141-143° (11 mm); n_D^{20} 1.5395; d_4^{20} 1.1030; MR_D 46.61; calculated 45.18.

0.1268 g sub.: 0.3415 g CO_2 ; 0.0851 g H_2O . 0.1679 g sub.: 25.46 ml CH_4 (0°, 760 mm). 0.1084, 0.2317 g sub.; 18.80 g benzene; Δt 0.185, 0.385°. Found %: C 73.45; H 7.53; OH 11.5; M 160.1, 164.5. $C_{10}H_{12}O_2$. Calculated %: C 73.17; H 7.31; OH 10.36; M 164.

Preparation of 2,7-Dimethylbenzofuran

2 g of the oxide of o-propenyl-o-cresol was placed in a desiccator over sulfuric acid. The liquid became mobile and acquired a brown color overnight. 1.4 g of a mobile yellowish liquid (X) was obtained by its distillation.

B.p. 72° (3 mm); n_D^{20} 1.5540; d_4^{20} 1.0440; MR_D 44.82; calculated 43.75.

0.1266 g sub.: 0.3808 g CO_2 ; 0.0777 g H_2O . 0.1217, 0.2197 g sub.; 18.9 g benzene; Δt 0.225, 0.416°. Found %: C 82.08; H 6.87; M 147.1, 143.4. $C_{10}H_{10}O$. Calculated %: C 82.10; H 6.85; M 146. A test for hydroxyl groups was negative.

Reaction of the Oxide of o-Propenyl-o-cresol with Acetic Anhydride

3 g of the oxide and 10 g of acetic anhydride were boiled for 4 hours. 1.0 g of a readily mobile liquid (X) was obtained by distilling the reaction products.

B.p. 70-71° (3 mm); n_D^{20} 1.5515; d_4^{20} 1.0375; MR_D 44.65; calculated 43.75. Found %: C 82.20; H 7.30. $C_{10}H_{10}O$. Calculated %: C 82.10; H 6.85.

SUMMARY

1. The α -oxides of the allyl ether of phenol, o-allylphenol, o-allyl-o-cresol, o-propenylphenol and o-propenyl-o-cresol were prepared by the oxidation of the allyl and propenyl derivatives of phenol with peroxyacetic acid.
2. The allylphenol oxides were not altered by the action of zinc chloride, while upon heating with acetic anhydride they were acetylated at the phenolic hydroxyl group with formation of oxidoacetates.
3. The oxides of o-propenylphenols yield cumarone derivatives as a result of the action of dehydrating substances. The formation of compounds of the furan series from oxides of the o-propenylphenols proceeds via a preliminary conversion of the oxides into their unsaturated tautomeric phenol alcohols.
4. The conversion of oxides of o-propenylphenols into cumarone derivatives confirms the presence of oxido-enolic tautomerism in the alcohol oxides.

LITERATURE CITED

- [1] V. I. Pansevich-Kolyada and L. I. Timoshek, J. Gen. Chem., 22, 1392 (1952). *

* See Consultants Bureau Translation, p. 1437.

- [2] V. I. Pansevich-Kolyada and L. A. Kureichik, *J. Gen. Chem.*, **24**, 231 (1954). *
- [3] V. I. Pansevich-Kolyada and V. A. Ablova, *J. Gen. Chem.*, **24**, 493 (1954). **
- [4] Claisen, *Eisleb Ann.*, **401**, 29 (1913); **418**, 78, 118 (1919).
- [5] K. A. Krasusky, *J. Russ. Chem. Soc.*, **34**, 537, 556 (1902); A. E. Favorsky, *J. Russ. Chem. Soc.*, **38**, 741 (1906).
- [6] Claisen, *Ann.*, **418**, 72 (1919); Lauer, *Leekly*, *J. Am. Chem. Soc.*, **61**, 3042 (1939).
- [7] Lipp, *Ber.*, **18**, 3282 (1885); **22**, 2567 (1889); Z. Pogorzelsky, *J. Russ. Chem. Soc.*, **30**, 977 (1898); A. Vasilyev, *J. Russ. Chem. Soc.*, **30**, 993 (1898); Henry, *Chem. Zentr.*, 1907, **1**, 708; Yu. S. Zalkind, *Ber.*, **56**, 189 (1923).
- [8] Claisen, *Ber.*, **53**, 324 (1920); *Ann.*, **418**, 84 (1919); Adams, Rindfusz, *J. Am. Chem. Soc.*, **41**, 655 (1919); F.G. Ponomarev, *J. Gen. Chem.*, **23**, 656 (1953); Stoermer, Barthelmess, *Ber.*, **48**, 67 (1915).
- [9] Claisen, *Eisleb Ann.*, **401**, 79 (1913).

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* See Consultants Bureau Translation, p. 231

** See Consultants Bureau Translation, p. 503.

*** See Consultants Bureau Translation, p. 681.

OXIDATION OF TERTIARY α -KETO ALCOHOLS BY MANGANESE TRIACETATE

S. Zonis

As the author and a coworker have shown [1], during the oxidation of α -glycols with manganese triacetate, rupture of the carbon skeleton occurs regardless of the character of the alcoholic groups; a mechanism was proposed for the reaction. To confirm the hypothetical mechanism we investigated the oxidation of secondary α -keto alcohols. If the formation of glycolate occurs as an intermediate product in the oxidation process, then the secondary α -keto alcohols should be oxidized with retention of the carbon skeleton (with formation of an α -diketone), even in the presence of excess oxidant; the tertiary α -keto alcohols, on the other hand, must be oxidized only with rupture of the carbon skeleton (with formation of neutral and acidic products).

Our investigations of the oxidation of tertiary α -keto alcohols of the aromatic phenylbenzoin and phenylanisoin series confirmed our hypotheses.

Diphenylketone and *p*-methoxydiphenylketone were isolated from the neutral reaction products as a result of the oxidation of these α -keto alcohols. Benzoic and anisic acid were isolated from the acidic products.

EXPERIMENTAL

Phenylbenzoin was prepared from benzil and phenylmagnesium bromide by the method described by S. Akri [2], with a m.p. of 86-87° (from ligroin).

Phenylanisoin was prepared from anisil and phenylmagnesium bromide. Inasmuch as phenylanisoin has not been described in the literature, we present the description of one of the experiments.

Phenylmagnesium bromide was prepared in the usual way from 1.3 g of magnesium and 9 g of bromobenzene. The phenylmagnesium bromide was added in the form of drops to a cooled ethereal solution of anisil (made from 7 g of anisil in 300 ml of anhydrous ether). Upon completion of the addition of the organomagnesium complex, the reaction mixture was stirred for 2 days at room temperature and then heated on a water bath for 1 hour. The warm ethereal solution was decanted from the unreacted anisil. The ethereal solution was dried with roasted sodium sulfate. After distilling off a portion of the ether, a yellow crystalline precipitate consisting of unreacted anisil settled out. Two substances were isolated from the filtrate by fractional crystallization — one with a m.p. of 86-95°, the other with a m.p. of 93-95°. After two-fold crystallization of the latter from methyl alcohol, crystals with a m.p. of 94-95.5° were isolated. A mixed sample with anisil melted (not sharply) at 85-115°.

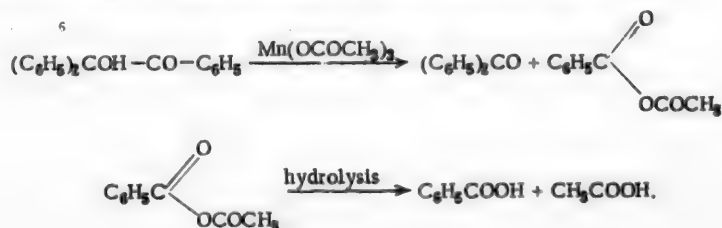
Analysis of the crystalline substance with a m.p. of 94-95°:

0.1258 g sub.: 0.3503 g CO₂; 0.0615 g H₂O. 0.3039 g sub.: 22.23 g benzene; Δt 0.204°: 0.1063 g sub.: 6.74 ml CH₄ (22°, 764.2 mm). Found %: C 75.95; H 5.47; M 335.8. C₂₂H₂₀O₄. Calculated %: C 75.86; H 5.74; M 348.0; 6.83 ml CH₄.

It can be concluded on the basis of the analytical data that the crystalline substance with a m.p. of 94-95.5° is phenylanisoin.

Oxidation of Phenylbenzoin

The equation of the oxidation reaction can be depicted by the following scheme:



We present the description of one of the experiments involving the oxidation of 1 g of phenylbenzoin with a m.p. of 86-87°, 2.4 g of manganese triacetate (68%) in 100 ml of glacial acetic acid.

The reaction mixture was heated on a boiling water bath for 10 hours and then a portion of the acetic acid (75 ml) was distilled off and the residue poured into water. The aqueous solution was neutralized with potash and steam distilled to isolate the neutral products. An ethereal extract was made from the aqueous distillate and after drying over sodium sulfate the ether was distilled off; 0.6 g of a viscous oily liquid was left in the flask. Upon seeding with a crystal of diphenylketone, the entire liquid crystallized, m.p. 47-48°. A mixed sample with known diphenylketone did not give any lowering of the melting temperature.

The aqueous solution left after distilling off the diphenylketone was acidified with nitric acid, and secondarily steam distilled to eliminate the acetic acid. A test with hydrogen peroxide and ferric chloride qualitatively disclosed the presence of benzoic acid in the distilled liquid.

After the steam distillation of the acetic acid, the aqueous solution left in the distilling flask was treated with ether to extract the benzoic acid. The ethereal extract was saturated with ammonia after drying over fused sodium sulfate and then treated with a concentrated solution of silver nitrate; the silver salt thereupon precipitated.

0.1697 g salt: 0.0803 g Ag. Found %: Ag 47.31. $C_7H_5O_2Ag$. Calculated %: Ag 47.13.

Oxidation of Phenylanisoin

The oxidation proceeds according to a scheme analogous to that for the oxidation of phenylbenzoin.

1.04 g of phenylanisoin with a m.p. of 94-95.5°, 2.1 g of manganese triacetate (68%) and 100 ml of glacial acetic acid were taken. The reaction conditions for the oxidation were the same as those for the oxidation of phenylbenzoin. After steam distillation, 0.52 g of a substance was isolated which crystallized from alcohol in the form of shiny needles, with a m.p. of 59.5-60.5°.

To characterize the p-methoxydiphenylketone, the oxime with a m.p. of 116-117° was prepared (from alcohol) by the usual method; its m.p. was in accord with the literature data [3].

The aqueous solution left after steam distilling the p-methoxydiphenylketone, was acidified with nitric acid and secondarily steam distilled to eliminate the acetic acid. Anisic acid which melted at 182-183° (from water) was left in the distilling flask after eliminating the acetic acid. According to the literature data, the melting point of anisic acid is 184.4° [4].

The anisic acid was converted into the silver salt to characterize it:

0.1679 g salt: 0.0702 g Ag. Found %: Ag 41.81. $C_8H_7O_3Ag$. Calculated %: Ag 41.68.

SUMMARY

Tertiary α -keto alcohols are oxidized only with rupture of the carbon skeleton, which is in accord with the reaction mechanism previously proposed.

LITERATURE CITED

- [1] S. Zonis and Yu. Kornilova, J. Gen. Chem., 20, 1252 (1950). *
- [2] S. Akri, Ber., 37, 2753 (1904).
- [3] R. Stoermer, Ber., 44, 667 (1911).
- [4] O. Flaschner. Monatsh., 31, 45 (1910).

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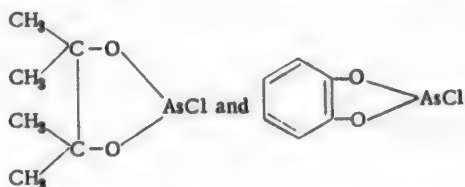
* See Consultants Bureau Translation, p. 1300

THE ACID CHLORIDES AND MIXED ESTERS OF TETRAMETHYLENEGLYCOLARSENOUS AND PYROCATECHOLARSENOUS ACIDS

Gilm Kamai and Z. L. Khisamova

Work on the synthesis of various cyclic acid chlorides and mixed esters of α -glycolarsenous and β -glycolarsenous acids [1,2] was begun in our laboratory in 1951.

In a continuation of this investigation, we synthesized the following cyclic acid chlorides for the first time:

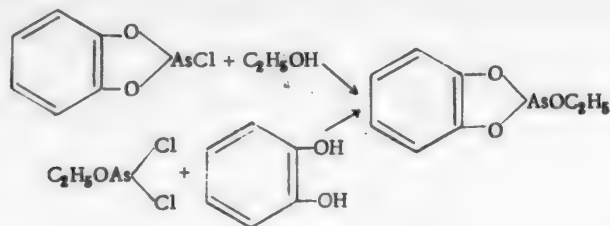


The acid chlorides isolated were crystalline substances, soluble in water and certain organic solvents. When kept for a long time, hydrolysis of the aqueous solutions of the acid chlorides occurs with formation of arsenous anhydride and the corresponding dihydroxy compounds.

We obtained mixed esters by the reaction of the indicated acid chlorides with various alcohols in the presence of substances which bind HCl. Certain data concerning them is set forth in the table.

No.	Formula	Boiling point	Melting point	d_4^{20}	n_D^{20}
1		—	94°	—	—
2		133° (8 mm)	—	1.2306	1.4622
3		116–117 (10 mm)	148–150	—	—
4		140–141 (14 mm)	—	1.3634	1.5400
5		164–165 (4.5 mm)	—	1.2241	1.5182
6		175–176 (5 mm)	—	1.2005	1.5150

For comparison, we synthesized the ethyl ester of pyrocatecholarsenous acid by the two following methods:



EXPERIMENTAL

Preparation of the Acid Chloride of Tetramethylethyleneglycolarsenous Acid

In a round-bottomed flask equipped with a reflux condenser, a mechanical stirrer and a dropping funnel, 44.3 g. of pinacol, 59.3 g. of anhydrous pyridine and 500 ml of anhydrous ether were placed. 67.6 g. of arsenic trichloride was added while the mixture was being externally cooled and stirred. After the addition of the entire quantity of arsenic trichloride, the contents of the flask were boiled on a water bath for 30 minutes. The precipitate was then filtered off and washed twice with ether. After the solvent had been distilled off, white crystals with a m.p. of 121° precipitated. The yield was 53.4%.

Found %: As 33.20, 33.23; Cl 15.77, 15.63. $C_6H_{12}O_2AsCl$. Calculated %: As 33.06; Cl 15.61.

The acid chloride of tetramethylethyleneglycolarsenous acid was quite soluble in water, acetone, benzene, chloroform, dioxane and more difficultly soluble in gasoline and xylene.

Saponification of the Acid Chloride of Tetramethylethyleneglycolarsenous Acid

1 g of the acid chloride was stirred with 30 ml of water and left overnight. On the next day the white precipitate which was formed was filtered off, washed with water, dried to constant weight and analyzed.

Found %: As 75.52, As_2O_3 . Calculated %: As 75.74.

Preparation of the n-Butyl Ester of Tetramethylethyleneglycolarsenous Acid

10 g of the acid chloride of tetramethylethyleneglycolarsenous acid was added through a dropping funnel to a solution of 3.62 g of n-butyl alcohol, 3.5 g of anhydrous pyridine and 300 ml of anhydrous ether. After the introduction of all the acid chloride, the contents of the flask were heated on a water bath. On the next day the precipitate — pyridine hydrochloride — was filtered off and washed with ether. After distilling off the solvent, the liquid which was left was vacuum distilled. A fraction with a b.p. of 170-190° at 12 mm, which crystallized on standing, was isolated. After recrystallization from toluene the m.p. was 94°.

Found %: As 28.46, 28.43. $C_{10}H_{21}O_3As$. Calculated %: As 28.36.

The ester isolated was soluble in many of the usual organic solvents. It hydrolyzed in water.

Preparation of the n-hexyl Ester of Tetramethylethyleneglycolarsenous Acid

The n-hexyl ester of tetramethylethyleneglycolarsenous acid was synthesized from 2.5 g of n-hexyl alcohol and 5 g of the acid chloride of tetramethylethyleneglycolarsenous acid in an ethyl ether medium in the presence of 1.75 g of pyridine.

B.p. 133° at 8 mm; d_4^{20} 1.2515; d_4^{25} 1.2306; n_D^{20} 1.4622.

Found: As 25.83, 25.72. $C_{12}H_{25}AsO_3$. Calculated %: As 25.63

The ester obtained consisted of a colorless liquid, soluble in many organic solvents.

It was comparatively readily saponified with water with the formation of arsenous anhydride.

Preparation of the Acid Chloride of Pyrocatecholarsenous Acid

15 g of pyrocatechol and 25.6 g of arsenic trichloride were placed in a round-bottomed flask equipped with a reflux condenser. The contents of the flask were heated on an oil bath for 5 hours. The hydrogen chloride which was evolved was trapped with water. The remaining mass was heated in a sealed tube at 200° for 3 hours. After cooling the tube was opened. A crystalline substance with a m.p. of 133° was obtained after recrystallization from toluene. The yield was 24.2 g (61%).

Found %: As 34.46, 34.53; Cl 16.48, 16.36. $C_6H_4O_2AsCl$. Calculated %: As 34.30; Cl 16.23.

The acid chloride obtained was quite soluble in water, ether, acetone, benzene, chloroform, dioxane, and more difficultly soluble in toluene, xylene, and gasoline. It was saponified very slowly by water.

Saponification of the Acid Chloride of Pyrocatecholarsenous Acid

A mixture of 1 g of the acid chloride and 30 ml of water was heated in a flask equipped with a reflux condenser for 6 hours. On the next day the white precipitate which was formed was filtered off, washed and dried to constant weight.

Found %: As 75.55, As_2O_3 . Calculated %: As 75.74

The presence of pyrocatechol was qualitatively detected in an aqueous solution.

Preparation of the Ethyl Ester of Pyrocatecholarsenous Acid

Experiment 1. 20 g of the acid chloride of pyrocatecholarsenous acid was added through a dropping funnel to a solution, cooled to 0° and stirred, of 5 g of anhydrous ethyl alcohol, 7.3 g of anhydrous pyridine and 350 ml of benzene. The contents of the flask were boiled on a water bath for 30 minutes. After cooling, the precipitate was filtered off and washed with benzene. The mass left after distilling off the benzene was then subjected to vacuum distillation. 9.6 g (46%) of a fraction with a b.p. of 114° at 10 mm was isolated. It crystallized on standing. The melting point of the crystals was 150°.

Found %: As 32.95, $\text{C}_8\text{H}_9\text{O}_3\text{As}$. Calculated %: As 32.85. Found: M 230.2 (by Rast's method).

$\text{C}_8\text{H}_9\text{O}_3\text{As}$. Calculated: 228.1.

Experiment 2. The ethyl ester of pyrocatecholarsenous acid was prepared by the mutual reaction of 7.4 g of pyrocatechol, 10.6 g of anhydrous pyridine and 12.8 g of ethoxydichloroarsine in an anhydrous ethyl ether medium. After the usual treatment of the reaction products and vacuum distillation, a basic fraction with a b. p. of 116-117° at 10-11 mm and a m.p. of 148-149° was isolated.

Found %: As 32.88, 32.79, $\text{C}_8\text{H}_9\text{O}_3\text{As}$. Calculated %: As 32.85;

The ethyl ester of pyrocatecholarsenous acid was soluble in many organic solvents.

Saponification of the Ethyl Ester of Pyrocatecholarsenous Acid

3 g of the ethyl ester of pyrocatecholarsenous acid was stirred with 50 ml of water. The saponification reaction proceeded energetically with the formation of a white precipitate. The presence of pyrocatechol was qualitatively detected in the aqueous solution. The precipitate was filtered off, washed several times with water and once with alcohol. After it had been dried to constant weight, it was analyzed.

Found %: As 75.49, As_2O_3 . Calculated %: As 75.73.

Preparation of the n-Butyl Ester of Pyrocatecholarsenous Acid

The compound was prepared by the mutual reaction of 4 g of n-butyl alcohol, 3.7 g of pyridine and 10 g of the acid chloride in a benzene medium. After treatment of the reaction products and vacuum distillation, 4.2 g (35.8%) of a colorless liquid was isolated. Water hydrolyzed it.

B. p. 140-141° at 14 mm; d_4^{20} 1.3837; d_4^{30} 1.3634; n_D^{20} 1.5400

Found %: As 28.94, 29.08, $\text{C}_{10}\text{H}_{13}\text{O}_3\text{As}$. Calculated %: As 29.25

Preparation of the n-Octylpyrocatechol Ester of Arsenous Acid

3.8 g of the n-octylpyrocatechol ester of arsenous acid was obtained in the form of a colorless liquid from 4 g of n-octyl alcohol, 2.5 g. of anhydrous pyridine and 6 g of the acid chloride in a benzene medium.

B. p. 164-165° at 4.5 mm; d_4^{20} 1.2426; d_4^{30} 1.2241; n_D^{20} 1.5182.

Found %: As 23.79, 23.81. $\text{C}_{14}\text{H}_{21}\text{O}_3\text{As}$. Calculated %: As 23.99.

Preparation of the n-Nonylpyrocatechol Ester of Arsenous Acid

4.5 g of n-nonyl alcohol, 2.5 g of anhydrous pyridine, 6.1 g of the acid chloride of pyrocatecholarsenous acid and 200 ml of benzene were taken for the reaction. After vacuum distillation, 4.2 g of a thick colorless liquid, quite soluble in organic solvents, was obtained.

B. p. 175-176° at 5 mm; d_4^{20} 1.2184; d_4^{30} 1.2005; n_D^{20} 1.5150. MR_D 81.94. $\text{C}_{15}\text{H}_{23}\text{O}_3\text{As}$. Calc. 81.53.

Found %: As 22.79, 22.85. $\text{C}_{15}\text{H}_{23}\text{O}_3\text{As}$. Calculated %: As 22.96.

SUMMARY

1. The acid chlorides of tetramethylethyleneglycolarsenous and pyrocatecholarsenous acids were prepared and studied for the first time.

2. By the reaction of these acid chlorides with various alcohols in a benzene medium and in the presence of anhydrous pyridine, the mixed esters of tetramethylethyleneglycolarsenous and pyrocatecholarsenous acids were synthesized and their properties described.

LITERATURE CITED

- [1] Gilm Kamal and Z. L. Khisamova, Proc. Acad. Sci. USSR, 535 (1951).
- [2] Gilm Kamal and Z. L. Khisamova. Proc. Acad. Sci. USSR, 81, 857 (1951); 86, 71 (1952); Bull. Acad. Sci. USSR, Div. Chem. Sci., 908 (1952).

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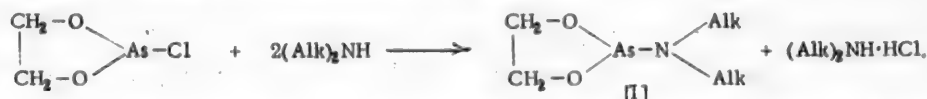
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THE REACTION OF CYCLIC ACID CHLORIDES OF ARSENOUS ACID WITH DIALKYLAMINES

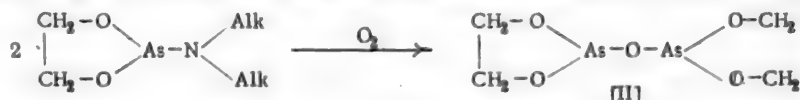
Gilm Kamai and Z. L. Khisamova

Substituted amido esters of arsenous acid with the $\text{As}-\text{N}$ bond have hitherto not been described. In the present communication, data are presented on the synthesis of the first few representatives of this group, of specifically cyclic dimethyl- and diethyl-substituted amido esters of arsenous acid.

We took the previously synthesized cyclic acid chlorides of ethyleneglycolarsenous, tetramethylethyleneglycolarsenous and pyrocatecholarsenous acids [1] as subjects for the investigation and let them react in an inert solvent with trimethylamine or diethylamine. In the reaction of the acid chloride of ethyleneglycolarsenous acid with dialkylamines in a medium of dry benzene, the reaction fundamentally goes in the direction of forming dialkyl-substituted amides of the cyclic esters of arsenous acid (I) according to the scheme:



It will also become clear that during this reaction, in addition to the dialkyl substituted amidoesters of arsenous acid, a considerable quantity of the ethyleneglycolic ester of pyroarsenous acid (II) was formed. The formation of the latter as an oxidation product with rupture of the $\text{As}-\text{N}$ bond can be represented by the following scheme:



We did not study the nitrogen-containing portion of this reaction in detail.

It is of interest to note that, in the reaction of the acid chlorides of tetramethylethyleneglycolarsenous and pyrocatecholarsenous acids with dialkylamines under analogous reaction conditions and in an atmosphere of air, we isolated only the corresponding esters of pyroarsenous acid.

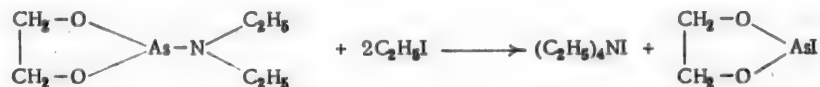
We accomplished the synthesis of dialkyl substituted amido esters of tetramethylethyleneglycolarsenous and pyrocatecholarsenous acids by the action of the corresponding acid chlorides on dialkylamines in a medium of inert solvent and in a stream of nitrogen.

The dialkyl-substituted amido esters of arsenous acid synthesized by us are presented in Table 1.

The amido esters isolated were colorless liquids. They were oxidized in air with rupture of the $\text{As}-\text{N}$ bond and formation of the corresponding esters of pyroarsenous acid (Table 2).

The pyroarsenous esters investigated were comparatively readily saponified by water.

We then studied the reaction between ethyl iodide and the diethylamido ester of ethyleneglycolarsenous acid. The experiments showed that the indicated substances react in the cold and in an ether medium according to the following scheme:



EXPERIMENTAL

Preparation of the Dimethylamide of Ethyleneglycolarsenous Acid

26.4 g of freshly distilled diethylamine and 100 ml of dry benzene were placed in a flask with a reflux condenser, mechanical stirrer and dropping funnel. The flask was externally cooled with snow. A solution of 50 g of the acid chloride of ethyleneglycolarsenous acid in 100 ml of benzene was added from the dropping funnel. Upon completion of the reaction, dimethylamine hydrochloride was separated by centrifuging.

The mass which was left after distilling off the benzene from the filtrate was subjected to vacuum distillation. Two fractions were isolated after 2-fold distillation.

The first fraction, 13.9 g (26.7%) consisted of a colorless, readily mobile liquid with a weak amine odor.

B. p. 101-102° at 55 mm; d_4^{20} 1.4643; n_D^{20} 1.5030; MR_D 36.14; Calc. 36.32.
Found %: As 41.57; N 7.35; $C_4H_{10}O_2AsN$. Calculated %: As 41.82; N 7.81.

The dimethylamide of ethyleneglycolarsenous acid was soluble in many organic solvents. It was hydrolyzed by water with the formation of arsenous anhydride.

The second fraction was a colorless, thick liquid with no odor:

B.p. 172-175° at 18 mm; d_4^{20} 2.0221; n_D^{20} 1.5569; MR_D 45.72; Calc. 45.42.
Found %: As 51.95, 51.89. $C_4H_5O_3As_2$. Calculated %: As 52.40.

The analytical data indicate that the second fraction was the comparatively pure ethyleneglycol ester of pyroarsenous acid (II). The ester was saponified by water with the formation of ethyleneglycol and arsenous anhydride.

TABLE 1

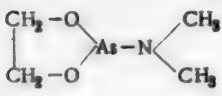
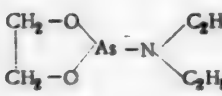
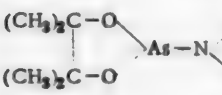
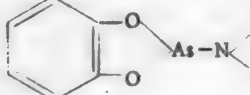
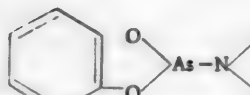
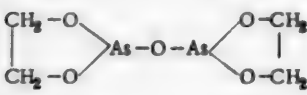
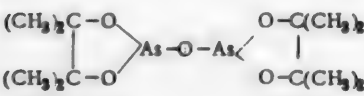
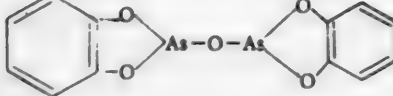
Formula	Boiling point at the given pressure (mm)	d_4^{20}	n_D^{20}	As (%)		N (%)		Yield (%)
				Calc.	Found	Calc.	Found	
	101-102° (55)	1.4643	1.5030	41.84	41.64	7.83	7.13	26.7
	85-86 (12)	1.3535	1.4948	36.10	36.11	6.57	6.79	58.0
	94 (16)	1.2345	1.4810	31.80	32.07	5.96	5.78	70.0
	146 (26)	1.4795	1.5868	33.00	32.76	—	—	26.3
	149 (17)	1.3620	1.5608	29.34	29.48	5.47	5.05	28.3

TABLE 2

Formula	Boiling point at pressure (mm)	Melting point	As (%)		Notes
			Calc.	Found	
	122-123° (1)	—	52.40	51.89	Liquid
	142 (3)	97°	37.42	37.39	Colorless Crystals
	—	147	39.0	38.79	Colorless Crystals

The preparation of the diethylamide of ethyleneglycolarsenous acid was carried out by the method described above, starting with 20 g of the acid chloride of ethyleneglycolarsenous acid, 17.2 g of diethylamine and 250 ml of ethyl ether. The following were obtained as a result of two-fold fractional distillation:

14.2 g of the first fraction. This consisted of a readily mobile colorless liquid which was soluble in many organic solvents. It was hydrolyzed by water:

B. p. 88-89° at 17 mm; d_4^{20} 1.3442; n_D^{20} 1.4918.

Found %: As 35.83; N 6.75. $C_8H_{14}O_2AsN$. Calculated %: As 36.10; N 6.98.

The second fraction:

B. p. 172-173° at 18 mm; d_4^{20} 2.0245; n_D^{20} 1.5569.

Found %: As 52.09. $C_4H_8O_3As_2$. Calculated %: As 52.40.

Thus, the ethyleneglycol ester of pyroarsenous acid was also isolated during this reaction.

Reaction of the diethylamide of ethyleneglycolarsenous acid with ethyl iodide.

4.3 g of ethyl iodide was added to a cooled mixture of 5.8 g of the diethylamide of ethyleneglycolarsenous acid and 50 ml of anhydrous ether which was placed in a small flask with a reflux condenser. After several minutes a crystalline precipitate began to settle out. On the next day the crystals were filtered off, washed with ether and dried to constant weight. The crystals were soluble in water and alcohol and insoluble in ether.

Found %: I 49.27, 49.19. $C_8H_{20}NI$. Calculated %: I 49.00.

Nitrogen was qualitatively detected; arsenic was absent. The compound obtained consisted of tetra-ethylammonium iodide according to the analytical data.

A fraction with a b.p. of 150-152° at 10 mm was separated by vacuum distilling from the liquid portion of the reaction products. We did not study the light yellow colored liquid in detail.

Reaction of the Acid Chlorides of Tetramethylethyleneglycolarsenous and Pyrocatecholarsenous acids with Dialkylamines

Experiment 1. 15.12 g of the acid chloride of tetramethylethyleneglycolarsenous acid, dissolved in benzene, was added to a stirred solution of 6 g of dimethylamine in 30 ml of dry benzene. The precipitate of dimethylamine hydrochloride which settled out was filtered off. After distilling off the solvent from the filtrate the mass which was left was subjected to vacuum fractional distillation. A fraction with a b.p. of 142° at 3 mm which rapidly crystallized was isolated. The crystals were soluble in many organic solvents. M.p. 97°.

Found %: As 37.39, 37.45. $C_{12}H_{24}O_6As_2$. Calculated %: As 37.63.

We did not succeed in isolating other individual substances.

Experiment 2. By the reaction of the corresponding quantities of the acid chloride and dimethylamine according to the method indicated above, but in a jet of nitrogen, a fraction was isolated in the form of a colorless liquid:

B. p. 94° at 16 mm; d_4^{20} 1.2345; n_D^{20} 1.4810; MR_D 54.22; Calc. 54.71

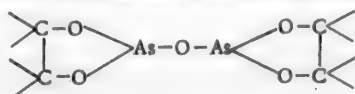
Found %: As 32.07; N 5.78. $C_8H_{18}O_2AsN$. Calculated %: As 31.86; N 5.96.

The preparation of the two dialkylamidopyrocatecholarsenous esters and the pyrocatechol ester of pyroarsenous acid was carried out according to the method described above.

The data on the esters obtained are set forth in Tables 1 and 2.

SUMMARY

1. Dialkyl substituted amides of the cyclic esters of arsenous acid were synthesized for the first time.
2. It was shown that the $\text{As}-\text{N}$ bond is very unstable in these compounds and is disrupted by the action of alkyl halide, atmospheric oxygen and water.
3. It was established that the product of the oxidation of the dialkylamido esters of arsenous acid consists of cyclic esters of pyroarsenous acid with the following composition:



LITERATURE CITED

[1] Gilm Kamai and Z. L. Khisamova, Proc. Acad. Sci. USSR, 46, 535 (1951); Gilm Kamai and N. A. Chadaeva, Proc. Acad. Sci. USSR, 81, 857 (1951); 86, 41 (1952).

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ALKYLATION OF BENZENE BY ALIPHATIC ALCOHOLS AND HALOGEN DERIVATIVES OVER ALUMINO - SILICATE CATALYSTS

B. N. Dolgov and A. S. Cherkasov

The number of published works devoted to the vapor phase catalytic alkylation of aromatic hydrocarbons by alcohols and alkyl halides is remarkably small. What has been investigated is chiefly alkylation with methyl and ethyl alcohols * and with methyl chloride. The yields of alkyl substituted aromatic hydrocarbons obtained by alkylation with these reagents at atmospheric pressure, does not exceed 10-15% of the theoretical yield [1,2,3]. Only by conducting the reaction under pressure was a yield up to 30% of the theoretical successfully obtained [4]. Vapor phase alkylation with alcohols and halogen derivatives is accomplished with the aid of catalysts, of which the most effective are the aluminosilicate : [1,2,3,5,6,7] and phosphoric acid or its salts [4,8,9].

From 1947 on, work on the study of the alkylation of aromatic hydrocarbons with alcohols and halogen derivatives over aluminosilicate catalysts has been carried out in the Department of Organic Chemistry at Leningrad University. The results obtained constitute the material for a bachelor's thesis presented by one of us in 1950. We investigated the alkylation of benzene with ethyl, n-propyl, isopropyl and isopropyl bromides, and isobutyl bromide. The alkylation was carried out over an aluminosilicate catalyst at atmospheric pressure in the usual apparatus used in the investigation of vapor phase catalytic reactions under dynamic conditions.

Alkylation with Alcohols

The reaction between benzene and isopropyl alcohol proceeds most readily. The reaction products are isopropylbenzene and polyalkylbenzenes (chiefly p-diisopropylbenzene), and also propylene and water which are formed as a result of the dehydration of isopropyl alcohol. Small quantities of saturated hydrocarbons (1-3%) and hydrogen (0.5-1.5%) are also contained in the gaseous reaction products, in addition to propylene. The formation of polyalkylbenzenes is markedly diminished by conducting the reaction with a great excess of benzene. Thus, the content of polyalkylbenzenes in the alkylbenzene fraction is equal to 20-30% at a molar ratio of benzene to alcohol of 2:1, while on increasing this ratio to 4:1, their content falls to 5-10%.

The optimal temperature for alkylating benzene with isopropyl alcohol is a temperature of 300-320° (Fig 1, curves I and II) at which the yield of isopropylbenzene reaches 52% of the theoretical (calculating on the basis of the alcohol passed) at a rate of supplying the reaction mixture (v) of 0.5 ml per 1 ml of catalyst per hour (curve I) and 60% at a rate of supply of 0.25 ml (curve II). Reducing the experimental temperature to 260° almost halves the rate of alkylation. Increasing the temperature above 320° also leads to a reduction in the yield of isopropylbenzene. Since no other new reaction products were formed in this case, while only the quantity of propylene formed was increased, it must be considered that at temperatures above 320° thermodynamic equilibrium is reached in our experiments between the starting materials and the reaction products. This is also confirmed by the fact that at temperatures of 340° and higher the yield of isopropylbenzene, obtained at a supply rate of 0.5 ml/ml per hour, is practically equal to the yield obtained at a rate of 0.25 ml/ml per hour.

The rate of the alkylation of benzene with n-propyl alcohol is somewhat less than the rate of alkylation with isopropyl alcohol: the yields of propylbenzene obtained at temperatures lower than the optimal (i.e., at temperatures at which the yield of propylbenzene is determined by the reaction rate and not by thermodynamic equilibrium) is always less in alkylation with n-propyl alcohol (Fig. 1, curve III). During alkylation with n-propyl alcohol, isomerization of the propyl group occurs in the course of the reaction, and it is not n-propylbenzene, but isopropylbenzene which appears as the reaction product, as in alkylation with isopropyl alcohol. On the basis of the fact that over aluminosilicate catalysts alcohols are readily dehydrated, being converted into olefins (isopropyl alcohol, for example, is practically completely dehydrated to propylene even at 240-250° [12] while olefins alkylate aromatic hydrocarbons over the same catalysts,

* Works by Turova-Polyak with her coworker [10] and Shuikin and his coworkers [11] have recently been published in which alkylation with higher alcohols has been investigated.

it seems very probable to us that alkylation with alcohols proceeds via intermediate formation of olefins. On the other hand, the fact that aromatic hydrocarbons can be alkylated with methyl alcohol indicates that a route of direct alkylation by alcohol which skips the stage of olefin formation, is not excluded. Actually, it is evident that both reactions can proceed parallelly in the alkylation with alcohols. If alkylation of benzene with alcohol proceeds only via intermediate olefin formation, then it must be expected that higher yields of alkylbenzene will be obtained in alkylation with olefins than in alkylation under the same conditions with the corresponding alcohols. The results of the experiments carried out by us involving the alkylation of benzene with propylene at various temperatures are presented in Fig. 1 (curve IV). As is evident from the data of the figure, at a temperature below 300° the yields of isopropylbenzene obtained in alkylation with propylene are actually higher than in alkylation with n-propyl alcohol. However, in alkylation with n-propyl alcohol at a temperature above 300°, and also in alkylation with isopropyl alcohol at various temperatures, higher yields are obtained than in alkylation with propylene. The difference in the yields of isopropylbenzene is particularly noticeable at low

TABLE 1

Expt. No.	Rate of supply of benzene (ml/ml/hr)	Amount of reaction mixture passed (g)	Yield of isopropylbenzene (%)
57a	0.4	17	42.5
57b	0.4	18	35.1
57c	0.4	17	26.9
58a	0.2	17	48.3
58b	0.2	17	37.1

Note: The temperature was 320°, the molar ratio $C_6H_6:C_3H_8 = 4:1$, the catalyst was 30 ml (9.5 g)

rates of supply of the reaction mixture (Fig. 2). Thus, at a rate of supply $v = 0.25$ ml/ml/hr and a temperature of 320° in alkylation with n-propyl and isopropyl alcohols, the yield of isopropylbenzene is equal to 58-60% (calculating on the basis of alcohol passed) as against 43% in alkylation with propylene. The small increase in the yield of isopropylbenzene (from 33 to 43%) at a 75% reduction in the rate of supply (from 1 to 0.25 ml/ml/hr) is characteristic of alkylation with propylene (Fig. 2, curve III), although the degree of conversion calculated for this temperature according to the reaction $C_6H_6 + C_3H_6 \rightleftharpoons C_6H_5C_3H_7$ is equal to about 80%. In our opinion, this fact is to be explained by rapid deactivation of the catalyst during the alkylation with propylene. The data presented in Table 1 are evidence of the presence of catalyst poisoning during alkylation with propylene. As is evident from the data of Table 1, after passing 17 g of a mixture of benzene with propylene over the catalyst, the yield of isopropylbenzene is lowered by 7-8% at a supply rate of benzene of 0.4 ml/ml/hr (experiments 57a, b, c) and by 11% at a rate of supply of benzene of 0.2 ml/ml/hr. After regeneration of the catalyst its activity is completely regenerated. The process of catalyst poisoning during alkylation with isopropyl alcohol proceeds considerably more slowly (Table 2, experiments 59a, b, 60a, b).

The yields of isopropylbenzene in alkylation with propylene over catalyst over which the alkylation with isopropyl alcohol has already been carried out, do not practically differ from the yields obtained for fresh or regenerated catalyst (experiments 59c and 60c). After carrying out alkylation with propylene, the catalyst also proved to be poisoned for the reaction of benzene with alcohol (experiments 59d and 60d).

We set up experiments in which the alcohol was decomposed over aluminosilicate catalyst by being passed through one oven and in which the propylene obtained, together with steam entered another oven to which benzene was also supplied. The yield of isopropylbenzene obtained by carrying out the experiments in this way, was no higher, and even somewhat lower (34%) than in the ordinary alkylation of benzene with propylene, i.e., the smaller poisoning and greater yield of isopropylbenzene in alkylation with alcohol in comparison with the yield obtained in alkylation with propylene, can evidently not be explained by the favorable reaction of steam with the direct product of the deactivation of the catalyst, which appears to be deposited on its surface of "coke" — highly unsaturated compounds which render the surface of the catalyst unsuitable for the reacting molecules. The formation of "coke", as has been shown

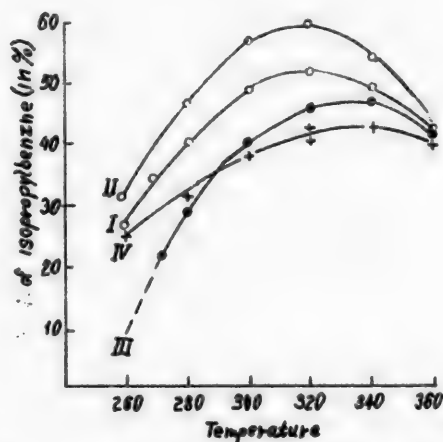


Fig. 1. I) Benzene + isopropyl alcohol, $v = 0.5$ ml/ml/hr; II) benzene + isopropyl alcohol, $v = 0.25$ ml/ml/hr; III) benzene + n-propyl alcohol, $v = 0.5$ ml/ml/hr; IV) benzene + propylene, $v = 0.5$ ml/ml/hr.

shown [13,14], is directly associated with the redistribution of hydrogen which proceeds readily during the contact of unsaturated hydrocarbons with aluminosilicate catalysts. Inasmuch as the rate of this reaction depends on the concentration of the unsaturated compounds (in our experiments on the concentration of propylene), which will be less in alkylation with alcohol than in alkylation with propylene, it can be assumed that the rate of deposition on the catalyst of substances which lead to its deactivation will also be less in alkylation with alcohol. It seems

to us that this circumstance is one of the causes which facilitate the preparation of higher yields of isopropylbenzene in the alkylation of benzene with alcohol, as compared with alkylation with propylene. In addition, in the first case, as has already been indicated, the formation of alkylbenzenes, evidently can proceed not only due to the reaction of benzene with the propylene which is formed by the dehydration of the alcohol, but also due to its direct condensation with alcohol. If these two reactions proceed parallelly, this will also facilitate higher yields of alkylbenzenes.

The alkylation of benzene with ethyl and butyl alcohols under conditions analogous to the conditions of the experiments involving the alkylation with propyl alcohols, hardly proceeds at all. In experiments with ethyl alcohol the yield of ethylbenzene amounted to about 4% of the theoretical; in alkylation with tertiary butyl alcohol only an insignificant quantity of tertiary butylbenzene was isolated; and in experiments with isobutyl alcohol no alkylbenzenes at all were obtained.

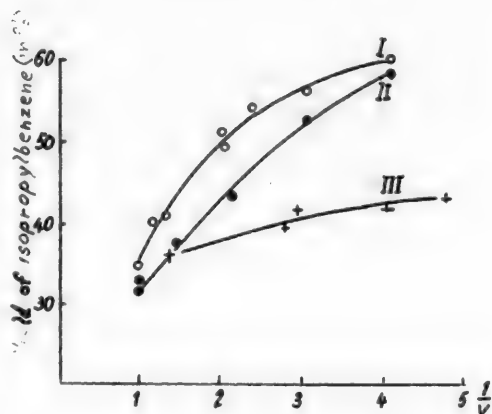


Fig. 2. I) Benzene and isopropyl alcohol; II) benzene + n-propyl alcohol; III) benzene + propylene. The temperature of the experiments was 320°; the molar ratio benzene : alcohol (propylene) = 4:1.

TABLE 2

Expt. No.	Alkylating agent	Rate of supply of the reaction mixture (benzene)	Amount of reaction mixture passed (g)	Yield of isopropylbenzene (%)
59a	iso-C ₃ H ₇ OH	0.5	16	48.2
59b	iso-C ₃ H ₇ OH	0.5	16	45.3
59c	CH ₃ CH=CH ₂	0.4	17	38.9
59d	iso-C ₃ H ₇ OH	0.5	16	23.5
60a	iso-C ₃ H ₇ OH	0.2	18	63.1
60b	iso-C ₃ H ₇ OH	0.2	18	60.0
60c	CH ₃ CH=CH ₂	0.2	17	44.5
60d	iso-C ₃ H ₇ OH	0.2	15	37.5
60e	CH ₃ CH=CH ₂	0.15	17	26.0

Note: The temperature was 320°, the molar ratio C₆H₆ : iso-C₃H₇OH = 4:1.

Alkylation with Alkyl Halides

It was found in the study of the alkylation of benzene with alkyl halides that high yields of alkylbenzenes were obtained only in the alkylations with isopropyl chloride, n-propyl bromide and isopropyl bromide. In the alkylation with ethyl bromide the yield of ethylbenzene amounted to not more than 10-15% of the theoretical, while in alkylation with isobutyl bromide only an insignificant quantity of tertiary butylbenzene was obtained.

Alkylation with isopropyl chloride, n-propyl bromide and isopropyl bromide was carried out at experi-

mental temperatures of 260 to 360°, a rate of supply of the reaction mixture of 0.5 ml/ml of catalyst per hour, and a molar ratio of benzene to alkyl halide of 4:1. Under these conditions the chief alkylation product was propylbenzene; the quantity of polyalkylbenzenes (chiefly p-diisopropylbenzene) amounted to 10-15% of the total weight of the alkylbenzene fraction. Alkylation with normal propyl bromide was accompanied by isomerization of the alkyl group and the reaction product was isopropylbenzene, just as in alkylation with isopropyl chloride and isopropyl bromide.

The experimental data, found by us for the dependence of the yield of isopropylbenzene (in percentages of the theoretical yield) on the experimental temperature in alkylation with various propyl halides, are graphically presented in Fig. 3. The curves obtained in the alkylation with isopropyl alcohol are also set forth for comparison.

As is evident from the data of Fig. 3, the alkylation of benzene with alkyl halides proceeds considerably more readily than alkylation with the corresponding alcohols: at 320° and a rate of 0.5 ml the yield of isopropylbenzene is equal to 59% in alkylation with isopropyl chloride, 67.5% with n-propyl bromide and 70-74% with isopropyl bromide as against 49-53% in alkylation with isopropyl alcohol. This difference in the rates of the alkylation reaction is particularly noticeable at an experimental temperature of 260°, at which the system is far removed from the equilibrium state. In this case, in alkylation with isopropyl alcohol the over-all yield of isopropylbenzene is equal to 27% of the theoretical, while in alkylation with isopropyl chloride it reaches 45% and with isopropyl bromide 60%.

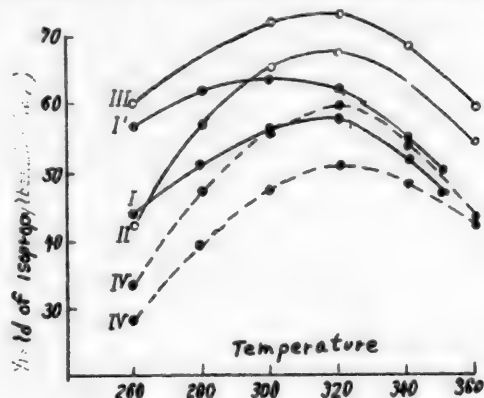


Fig. 3. I) Benzene + isopropyl chloride, $v = 0.5$ ml/ml per hour; I') benzene + isopropyl chloride, $v = 0.25$ ml/ml per hour, II) benzene + n-propyl bromide, $v = 0.5$ ml/ml per hour, III) benzene + isopropyl bromide, $v = 0.5$ ml/ml per hour; IV) benzene + isopropyl alcohol, $v = 0.5$ ml/ml per hour, IV') benzene + isopropyl alcohol, $v = 0.24$ ml/ml per hour.

At a temperature above 320° the curves which represent the results of the alkylation with isopropyl chloride, and with isopropyl alcohol, practically coincide. This is evidently to be explained by the fact that under these conditions the yield of isopropylbenzene is still determined by the thermodynamic equilibrium between isopropylbenzene, benzene and propylene. Carrying out the alkylation with n-propyl bromide and isopropyl bromide at a temperature above 320° also leads to lowering the yield of isopropylbenzene; however at temperature of 340 and 360° it still remains higher by 10-15% than in alkylation with isopropyl alcohol and isopropyl chloride. This difference, evidently, is to be explained by the greater rate of the direct alkylation reaction of benzene with propyl bromide in comparison with the reactions of the decomposition of propyl bromide into propylene and hydrogen bromide and the decomposition of isopropyl bromide into benzene and propylene. Only the fact that the catalytic decomposition of alkylbromides with formation of propylene proceeds more difficultly at higher temperatures than the decomposition of alkylchlorides, and, that the decomposition of the latter proceeds more difficultly than the decomposition of alcohols, is evidence that the direct alkylation reaction (without intermediate formation of unsaturated compounds) is possible. The very yields of isopropylbenzene which we obtain are higher in sum in the alkylation with isopropyl bromide, less in alkylation with isopropyl chloride and still less in alkylation with isopropyl alcohol. In addition, we also obtained direct evidence that alkylation with propyl bromides at temperatures below 260° proceeds without intermediate formation of unsaturated compounds.

We previously noted that during the alkylation of benzene with propylene, a rapid lowering of the activity of the catalyst occurs, and it also becomes slightly active in the alkylation with isopropyl alcohol. The situation is otherwise in alkylation with isopropyl bromide (Table 3).

As is evident from the data of Table 3, the yield of isopropylbenzene in alkylation with isopropyl bromide after passing over the catalyst (10 g), 42.5 g of a mixture of propylene and benzene (experiments 97c and 97d), or 25.4 g of a mixture of propylene and benzene and 24.1 g of a mixture of isopropyl alcohol and benzene, (experiments 98b and 98c) is diminished by a total of 5-8%. In alkylation with the same alcohol, even after passing 20-25 g of a mixture of propylene and benzene, the yield of isopropylbenzene falls by 20-22%. The high yield in the experiments with isopropyl bromide can not be explained by the freeing of the surface of the catalyst from products which cause its deactivation after alkylation with propylene. Evidence concerning this is furnished by the results of experiment 98e, in which the yield of isopropylbenzene is equal in all to 23.2%, i.e., carrying out the alkylation with isopropyl bromide (experiment 98d) does not improve upon the yield in alkyl-

ation with isopropyl alcohol.

TABLE 3

Experiment No.	Alkylating Agent	Amount of reaction mixture passed (g)	Yield of isopropylbenzene (%)
97a	iso-C ₃ H ₇ Br	25.3	68.2
97b	iso-C ₃ H ₇ Br	23.0	66.6
97c	CH ₃ CH=CH ₂	21.0	29.7
97d	CH ₃ CH=CH ₂	21.5	21.9
97e	iso-C ₃ H ₇ Br	20.5	62.7
98a	iso-C ₃ H ₇ Br	25.7	73.0
98b	CH ₃ CH=CH ₂	25.4	35.0
98c	iso-C ₃ H ₇ OH	24.1	26.9
98d	iso-C ₃ H ₇ Br	25.2	65.2
98e	iso-C ₃ H ₇ OH	25.0	23.2

Note: The temperature was 320°, the rate of supply of the reaction mixture, 0.5 ml/ml per hour and the catalyst 30 ml (10 g).

TABLE 4

Physico Chemical Constants of the Alkylbenzenes Obtained

Alkylbenzene	Boiling point	d ₄ ²⁰	n _D ²⁰	MR _D		Molecular weight		M.p. of the acetamido derivatives*	Alkylating agent
				Found	Calc.	Found	Calc.		
Isopropylbenzene	149-151*	0.8634	1.4914	40.3	40.2	122, 124	120	105-105.5	Isopropyl alcohol
Isopropylbenzene	149-151	0.8630	1.4912	40.3	40.2	121, 120	120	105-105.5	n-Propyl alcohol
Isopropylbenzene	148-151	0.8626	1.4912	40.4	40.2	118, 119	120	104-105	Propylene
Isopropylbenzene	149-152	0.8628	1.4915	40.4	40.2	124, 120	120	105.5-106	Isopropyl chloride
Isopropylbenzene	150-153	0.8623	1.4912	40.4	40.2	121, 118	120	104-105	Isopropyl bromide
Isopropylbenzene	149-151	0.8628	0.4910	40.3	40.2	121, 117	120	104.5-105.5	n-Propyl bromide
Ethylbenzene	132-138	0.8701	1.4956	—	—	116, 114	106	225-225.5**	Ethyl alcohol
Ethylbenzene	131-136	0.8694	1.4953	35.6	35.5	106, 108	106	225-225.5**	Ethyl bromide
Tertiary-butylbenzene	162-170	0.8707	1.4879	44.8	44.8	130, 127	134	168-169.5	Tertiary-butyl alcohol
Tertiary-butylbenzene***	160-170	0.8854	1.4863	—	—	128, 126	134	167-168	Isobutyl bromide

* The acetamido derivatives were prepared by the method of Ipatieff and Schmerling [15].

** The melting point presented is that of the diacetamido derivatives.

*** A test (Beilstein's method) showed the presence of halogen.

To explain the high yields of isopropylbenzene in the reaction of isopropyl bromide with benzene after the catalyst appears to a considerable extent poisoned for alkylation with propylene and isopropyl alcohol, the following hypotheses can be proposed:

1) Less activation energy is required for alkylation of benzene with isopropyl bromide than for alkylation

with propylene and isopropyl alcohol, i.e., the first reaction proceeds readily after the deactivation of the most active centers of the catalyst, on which the alkylations of benzene with propylene and alcohol proceed.

2) The alkylation of benzene with propylene and with alcohol, and the alkylation with isopropyl bromide proceed on different kinds of active centers; the transformation products of propylene poison the active centers on which the first two alkylation reactions proceed.

The first hypothesis seems more probable to us. Further research is required for the final solution of this problem.

Identification of the Alkylation Products

The liquid reaction products were distilled in a fractionating column. The constants of the monoalkylbenzenes are presented in Table 4.

In addition to monoalkylbenzenes, diisopropylbenzene was isolated from the combined high-boiling fractions obtained in the experiments with propyl alcohols and propyl bromides:

B. p. 200-206°; d_4^{20} 0.8608; n_D^{20} 1.4910; MR_D 54.6; M 162, 156. $C_6H_4(C_3H_7)_2$.
Calculated: MR_D 54.0; M 162

To determine the position of the propyl groups in the diisopropylbenzene, 2 g of it was acidified by boiling with 20% nitric acid. Terephthalic acid was obtained as a result of the oxidation; this was proved by preparing a dimethyl ester from it which had a m.p. of 140°.

SUMMARY

1. An investigation of the alkylation of benzene with alcohols and halogen derivatives of the fatty series over aluminosilicate catalyst was carried out.

2. It was established that at a molar ratio of benzene to alkylating reagent of 4:1, the reaction products are basically monoalkylbenzenes.

3. The highest yields of alkylation products were obtained in alkylation with propyl alcohols and with propyl halides. Under optimal conditions (temperature 300-320°, a rate of supply of the reaction mixture of 0.25-0.5 ml per ml of catalyst per hour), the yield of propylbenzene amounts in alkylation with isopropyl alcohol to 50-60% of the theoretical, with n-propyl alcohol to 45-58%, with isopropyl chloride to 58-63%, with n-propyl bromide to 67% and with isopropyl bromide to 70-74%. The formation of alkylbenzenes is insignificantly small in alkylation with ethyl, isobutyl and tertiary-butyl alcohols, with ethyl bromide and with isobutyl bromide.

4. Alkylation of benzene with n-propyl alcohol and n-propyl bromide is accompanied by isomerization of the alkyl group and the reaction product is isopropylbenzene. In alkylation with isobutyl bromide, tertiary-butylbenzene is obtained.

5. In alkylation with propylene, the activity of the catalyst is quickly lowered in the course of the experiment. The reduction in catalyst activity in alkylation with alcohols and alkyl halides proceeds considerably more slowly. Catalyst which has been deactivated for alkylation with propylene, is not active for alkylation with alcohols either, but remains active for alkylation with alkyl halides.

LITERATURE CITED

- [1] P. Given, D. Hammick, J. Chem. Soc., 1947, 928.
- [2] N. Cullinnane, S. Chard, R. Meatjard, J. Soc. Chem. Ind., 67, 232 (1948);
- [3] N. Cullinnane, S. Chard, J. Chem. Soc., 1948, 804.
- [4] L. Erichsen, Angew. Chem., 61, 322 (1949).
- [5] L. Natanson, M. Ya. Kagan, J. Phys. Chem., 17, 381 (1943).
- [6] C. Thomas, V. Haensel, U. S. Patent 2384505 (1945)
- [7] Kutz, Corson, J. Am. Chem. Soc., 67, 1312 (1945).
- [8] Oil and Gas Journal, 41, No. 13 (1942).
- [9] U. S. Patents 2405874 (1946), 2409802 (1946), 2412230 (1946), 2442878 (1948), 2447599 (1948); British Patents 577314 (1946), 574738 (1946).

- [10] M. B. Turova-Polyak, G. I. Levi, L. M. Volkova and M. I. Kuimova, Proc. Acad. Sci. USSR, 89, 495 (1953)
- [11] N. I. Shuikin, A. B. Kuchkarev, N. A. Pozdnyak, Proc. Acad. Sci. USSR, 92, 785 (1953).
- [12] A. S. Nekrasov, B. A. Krentsel, J. Gen Chem., 19, 948 (1949). *
- [13] A. A. Mikhnovskaya, A. V. Frost, Proc. Acad. Sci. USSR, 37, 252 (1942).
- [14] A. A. Petrov, A. V. Frost, Proc. Acad. Sci. USSR, 55, 851 (1949).
- [15] V. N. Ipatieff, L. Schmerling, J. Am. Chem. Soc., 59, 1056 (1937).

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KINETICS OF THE HYDROGENATION OF THE BENZYL ESTER OF CINNAMIC ACID ON A POROUS NICKEL CATALYST

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The hydrogenation of the ethylenic bond in the benzyl ester of cinnamic acid has heretofore hardly been studied at all. The hydrogenation of the benzyl ester of cinnamic acid on a Ni catalyst on a silica gel, to which osmium was added, was studied in the work of Sokolsky and Vyugova [1].

In the present work, experimental material pertaining to the study of the influence of the rate of mixing on the rate of hydrogenation of the benzyl ester of cinnamic acid at 0, 25, and 40° is presented. It has been shown that the intensity of mixing during the preliminary saturation of the catalyst with hydrogen plays a decisive role in the formation of the porous nickel catalyst with a standard dispersion; consequently in the study of the dependence of the reaction rate on the rate of mixing, it occurred to us to saturate the catalyst with hydrogen under maximally intense conditions of mixing. Observation of this condition in the preparation of the catalyst permitted the demarcation of the diffusion and kinetic regions of the course of the reaction to be carried out more readily.

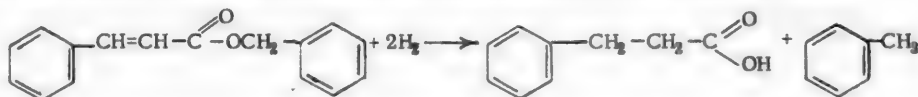
EXPERIMENTAL

The study of the kinetics of the hydrogenation of the benzyl ester of cinnamic acid was carried out with a chemically pure "Kahlbaum" brand preparation with a m.p. of 39° that was in complete agreement with the literature data.

The catalyst was prepared by leaching grains of a Ni - Al alloy with a content of 50% Ni [dimensions of the grains 0.2-0.4 mm (No. 1) or 0.4 - 1 mm (No. 2)] with 20% NaOH on a boiling water bath for 2 hours, after which the catalyst was washed with water and alcohol.

96% Ethyl alcohol was used as the solvent. Electrolytic hydrogen was used for the hydrogenation. The apparatus and experimental methods have previously been described by us [2].

The hydrogenation of the benzyl ester of cinnamic acid in the liquid phase, in all probability, can proceed with the formation of hydrocinnamic acid and toluene according to the following scheme:



To establish the direction of the hydrogenation of the ester on the porous nickel, an experiment was carried out in which a sample of the benzyl ester of cinnamic acid amounted to 60 g. The catalyst was prepared by leaching 15 g of Ni-Al alloy (with a content of 30% Ni).

200 ml of 96% ethyl alcohol and 60 g of ether were added to the catalyst.

The hydrogenation was carried out in a glass vessel, 0.5 liters in volume, at room temperature.

8.8 liters of hydrogen (11.3 liters were necessary according to the calculation) was consumed in the hydrogenation of 60 g of the ester after 675 minutes, after which the experiment was discontinued. After completion of the experiment, the catalyst was filtered off. The catalyzate in ethyl alcohol solution had the characteristic odor of toluene. Upon addition of bromine water to a portion of the catalyzate (2-3 ml), the bromine water was not decolorized, which indicated the absence of an unsaturated bond. The constant-boiling mixture of alcohol and toluene, 215 ml of which was formed as a result of the hydrogenolysis, was then distilled off.

100 ml of water was added to the same quantity of this mixture; the mixture was then intensively extracted. After separating the two layers the upper layer was dried over CaCl_2 and fractionated. 6 ml of toluene was thereby obtained. Thus, $6 \cdot 2.15 = 12.9$ ml of toluene can be isolated from 215 ml of the mixture, which corresponds (according to the hydrogen consumption) to the calculated quantity of toluene. Water was added to the residue in the distillation flask (evidently, a mixture of hydrocinnamic acid and the benzyl ester of hydrocinnamic acid) and the mixture was heated to 100°. Hydrocinnamic acid was isolated from the solution, and after washing with cold water and drying, was characterized by a m.p. of 48.5°, which is in accord with the literature data for hydrocinnamic acid and confirms the reaction course indicated by us.

The kinetics of the hydrogenation of the ester at various temperatures was studied in subsequent experiments. The kinetic hydrogenation curves and the results of these experiments are presented in Fig. 1 and Table 1.

As is evident from curve I (Fig. 1), the hydrogenation of the ester at 0° proceeds almost as a first order reaction, and the reactions, with an absorption of hydrogen of 62% of the theoretical, necessarily proceed at immeasurably slow rates. This inhibition of the reaction is apparently caused by the formation of the benzyl ester of hydrocinnamic acid, which is slightly soluble under these conditions and blocks the active nickel surface. Experiments carried out at 25° (curves II and III), showed that the hydrogenation of the ester was a mixed order reaction. Up to the absorption of 56.0% of the theoretical quantity of hydrogen, the order of the reaction is necessarily fractional (convex curves) and then, on further absorption of hydrogen, the curves acquire a linear character. In almost all cases, the reaction does not proceed to conclusion, since it proceeds for a long time at immeasurably small rates.

In our case, a certain selectivity of the process on the porous nickel at 25° is evidence of the mixed order of the reaction. It can doubtless be considered that the hydrogenation of the $-\text{CH}=\text{CH}-$ bond in the benzyl ester of cinnamic acid proceeds initially. The results of hydrogenation of a 60 g sample of the ester also lead to this conclusion; in the given case, the presence of the $-\text{CH}=\text{CH}-$ bond was not detected (with bromine water) after the absorption of 77% of the theoretically necessary hydrogen.

TABLE 1

Influence of the Temperature on the Rate of Hydrogenation of the Benzyl Ester of Cinnamic Acid on Porous Nickel

0.56 g of porous nickel (No. 2); 0.5 g of the ester; 25 ml of 96% alcohol. The catalyst was preliminarily saturated with H_2 for 15 min. The rate of mixing was 840 rocking oscillations per minute.

Experiment No.	Temperature	Order of the reaction	$1/2 V_0 \text{ H}_2$ after t minutes	$(\Delta V_0 / \Delta t)_{\text{av. up}}$ to the absorption of $1/2 V_0 \text{ H}_2$	K_t for hydrogenolysis	Quantity of H_2 absorbed in the hydrogenation (ml)
150	0°	First	36.0	1.3	—	58.0
128	25	Mixed	10.0	4.7	0.016	82.4
129*	25	Mixed	10.0	4.7	0.016	83.1
135	40	Mixed	7.0	6.6	0.041	84.6
145	50	Mixed	7.0	6.6	0.036	85.0
136**	25	Mixed	23.5	6.0	0.010	220.0

* Repetition of experiment 128

** The ester sample weighed 1.5 g.

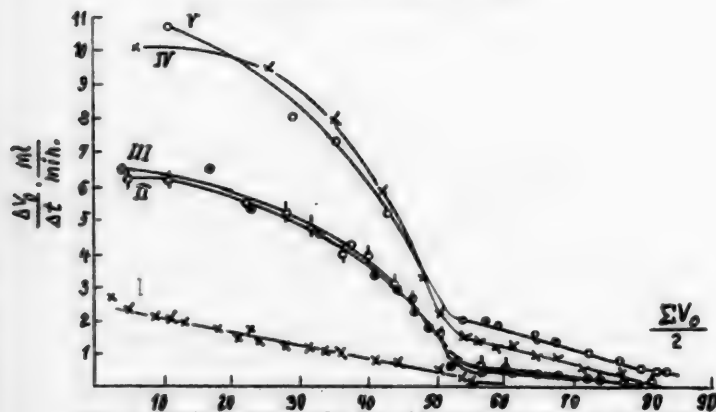


Fig. 1. Hydrogenation of 0.5 g of the benzyl ester of cinnamic acid at various temperatures. Explanation in the text.

The order of the reaction was not changed by raising the temperature to 40-50° (Fig. 1, curves IV and V). This circumstance indicated that the selectivity of the hydrogenation of the ester within the limits studied by us did not depend on the temperature. It follows that rate of hydrogenation of the $-\text{HC}=\text{CH}-$ bond is characterized by the time for half-hydrogenation and the average rate, while the hydrogenolysis is characterized by the rate constant of a first order reaction.

As is evident from the data of Table 1, raising the temperature to 50° does not lead to increase in the rate of the first process and even rather delays the second. The rate constant of hydrogenolysis at 50° was equal to 0.036. In addition, at 50° a considerable scattering of points is observed on the kinetic curve (curve V).

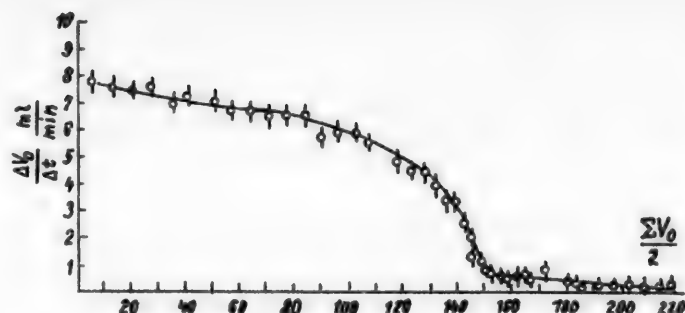


Fig. 2. Hydrogenation of 1.5 g of the benzyl ester of cinnamic acid.

The kinetic curve for the hydrogenation of a three-fold sample (1.5 g) of the ester of cinnamic acid at 25° (Table 1, experiment 136) is presented in Fig. 2. The kinetics of the reaction also correspond to that of a mixed order reaction in this case. Increase in the concentration of the hydrogenated substance leads to some increase in the rate of hydrogenation of the $-\text{CH}=\text{CH}-$ bond, which is characteristic for a fractional order reaction in an unsaturated compound. The rate constant of the hydrogenolysis with increase from 0.5 to 1.5 g in the sample of the substance being hydrogenated on the average remains constant and equal to 0.01.

In subsequent experiments we studied the dependence of the rate of hydrogenation of the benzyl ester of cinnamic acid on the rate at which the reaction mixture was shaken. With this object, two series of experiments were conducted. In the first series, preliminary saturation of the catalyst with hydrogen was carried out at the same intensity of mixing as in the hydrogenation; in the second series, the preliminary saturation of the catalyst with hydrogen was brought about with a maximum intensity of shaking. The results of these experiments are shown in Table 2 and Fig. 3.

The results presented in Table 2 show that with increased intensity of shaking in the range from 540 to 1340 rocking oscillations per minute during both the preliminary saturation of the catalyst with hydrogen and during the hydrogenation, a steady increase in the reaction rate occurs. As regards the hydrogenolysis constant, it remains almost constant both at small, and at considerable rates of mixing (within the limits studied by us) and is equal in the first case to 0.025 and in the second to 0.020. This phenomenon, apparently, is caused by sufficient dispersion of the catalyst in the process of hydrogenation of the $-\text{CH}=\text{CH}-$ bond.

TABLE 2

Influence of the Intensity of Mixing on the Rate of Hydrogenation of the Benzyl Ester of Cinnamic Acid

Temperature 25°; 0.56 g of porous nickel (No. 2); 0.5 g of the benzyl ester of cinnamic acid; 25 ml of 96% alcohol. The preliminary saturation of the catalyst with hydrogen was carried out for 15-20 minutes. The order of the reaction was mixed in all cases.

Experiment No.	Rate of shaking during the preliminary saturation of the catalyst (number of rocking oscillations per minute)	Number of rocking oscillations per minute during the hydrogenation.	Half hydrogenation time (minutes)	$(\Delta V_0 / \Delta t)_{\text{av}}$ up to the absorption of $1/2 V_0 \text{ H}_2$	K_{25} for hydrogenolysis
201*	216	216	11.0	4.3	0.030
202*	250	250	11.0	4.3	0.020
203*	320	320	10.0	4.7	0.026
204*	400	400	9.5	5.0	0.025
144	540	540	16.0	2.9	0.020
140	680	680	16.0	2.9	0.017
128	840	840	10.0	4.7	0.020
129**	840	840	10.0	4.7	0.020
141	1070	1070	9.5	4.9	0.020
142	1220	1220	8.0	5.9	0.021
143	1340	1340	8.0	5.9	0.020

* The experiments were carried out with porous Ni (No. 1), prepared from a 50% very finely ground alloy (powder type).

** Repetition of experiment 128

In this connection, it is curious that experiments Nos. 201-204, carried out with porous nickel from a very finely divided alloy (powder type), exhibited a very feeble dependence of the rate of hydrogenation on the intensity of mixing (from 216 to 400 rocking oscillations per minute).

In the aggregate, these data indicate the essential role of the so-called "secondary crystalline formations", which, as Rubinshtein [3] showed, consist of blocks and druses of the primary crystals and determine such properties of the catalyst as its specific surface, density, porosity and the character of the aggregation of the "primary crystals".

In connection with the question under consideration of the influence of the rate of mixing on the rate of hydrogenation, it is impossible to ignore the physical state of the "secondary crystalline formations", i.e., the dispersion of the catalyst. The dispersion of the catalyst is undoubtedly directly dependent on the conditions of the stirring; consequently varying intensity of the mixing during the preliminary saturation of the catalyst with hydrogen creates irregular conditions for the genesis of the porous nickel.

In this connection it was of interest to study the influence of the rate of mixing on the rate of hydrogenation of the ester with a strictly standard catalyst. This study was carried out at 0, 25, and 40°. In these experiments the preliminary saturation of the catalyst with hydrogen was carried out with a greater intensity of the shaking of the "duck" (1080 rocking oscillations per minute). The intensity of the shaking of the reaction mixture during the hydrogenation varied from 200 to 1320 rocking oscillations of the "duck" per minute. The experimental data are presented in Fig. 3.

In comparing the experimental results presented in Table 2, with the results presented in Fig. 3, it is not difficult to note the substantial influence of the rate of the mixing during the preliminary saturation of the catalyst with hydrogen on the rate of hydrogenation of the ester.

It is not possible to set a boundary for the conversion of the "diffusion" region into the "kinetic" region from the data of the first series of experiments (Table 2).

The dispersion of the catalyst is constant under conditions of maximum intensity of shaking of the mixture during the preliminary saturation of the catalyst with hydrogen (Fig. 3). This circumstance permits the demarcation of the regions of the reaction to be carried out graphically; if the process is carried out in the "kinetic" region, the reaction rate is characterized by a constant value.

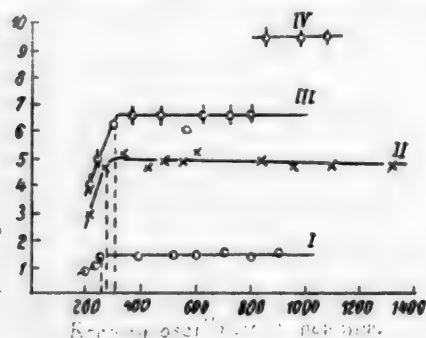


Fig. 3. Influence of the rate of mixing on the rate of hydrogenation of the benzyl ester of cinnamic acid at various temperatures. I) 0° II) 25° III) 40° IV) 40° (Ni No. 2).

The hydrogenolysis constant does not depend on the rate of mixing in the ranges studied by us and corresponds at a temperature of 25° to a value of 0.016 and at 40°, to 0.040. The apparent activation energy of the hydrogenolysis in this temperature range proved to be equal to 13950 cal/mole.

The position of the transition boundary of the "diffusion" region into the "kinetic" region depending on the temperature is noteworthy. As the curves show (Fig. 3), this transition is brought about at greater rates of stirring at higher temperatures. Thus, at 0° the transition boundary is found at about 250, at 25°, at around 270, and at 40°, at around 300 rocking oscillations per minute.

We also found a similar rule in the hydrogenation of dimethylacetylenylcarbinol [2]; this is completely explicable if one takes account of the fact that the temperature coefficient of the reaction is considerably higher than the temperature coefficient of diffusion. The difference in the temperature coefficients in the "diffusion" and in the "kinetic" regions was shown in the case of sunflower oil in the work of Elovich and Zhabrova [4].

The data presented in Fig. 3, permit the calculation by the Arrhenius formula of the apparent activation energy in the "diffusion" and "kinetic" regions. The results of these calculations are placed in Table 3.

It is evident from the data of Table 3, that at a comparatively low temperature, (0 - 25°), both in the "diffusion" and in the "kinetic" regions, the temperature coefficient is considerable and the value of the apparent activation energy corresponding to it is 6880 cal/mole in the "diffusion" region and 7960 cal/mole in the kinetic region. At higher temperatures (25-40°) the temperature coefficient has a lower value both in the "diffusion" and in the "kinetic" regions; the apparent activation energy in the "diffusion" region is characterized

by a value of 3900 cal /mole and in the "kinetic", by 4400 cal/mole.

TABLE 3

Reaction region and rate of mixing	$(\Delta V_0 / \Delta t)_{av}$ (in ml/minute) up to the absorption of 1/2 V_0 H_2 at the given temperature				Apparent activation energy (\pm 500 cal / mole) in the given temperature range		
	0°	25°	40°	50°	0-25°	25-40°	40-50°
Diffusion region, 210 rocking oscillations per minute.	0.9	2.9	4.5	—	6880	3900	—
Kinetic region, 800 rocking oscillations per minute	1.4	4.8	6.7	6.7	7960	4400	0

The activation energy for hydrogenation of the $-CH=CH-$ bond, calculated in the temperature range 40-50° (in the "kinetic" region), is equal to zero.

The diminution of the temperature coefficient of the reaction may be a result of the fact that with increase in temperature, the ratio of concentrations of the reacting components changes at the surface of the catalyst. To confirm this, it would be necessary to use the potentiometric method of investigation which makes it possible to measure accurately the concentration of one of the reacting substances on a surface [5].

SUMMARY

1. It was established that the hydrogenation of the benzyl ester of cinnamic acid proceeds with rupture of the $O-C$ bond at room temperature on porous nickel, and the reaction products are toluene and hydrocinnamic acid.
2. It was shown that the rate of hydrogenation of the ester up to the absorption of 56% of the theoretical quantity of hydrogen is comparatively great — under these conditions the hydrogenation of the $-CH=CH-$ bond proceeds; hydrogenolysis proceeds at low rates.
3. The influence of the rate of mixing on the rate of hydrogenation of the ester at 0, 25, and 40° was studied. It was shown that the intensity of mixing in the preliminary saturation of the catalyst with hydrogen plays a decisive role in the genesis of the catalyst.
4. With the use of the mixing factor, demarcation of the "diffusion" and "kinetic" regions of hydrogenation of the $-CH=CH-$ bond at various temperatures was carried out. It was established that the hydrogenolysis constant at 25 and 40° does not depend on the rate of stirring (in the limits of 200 - 1320 rocking oscillations per minute of the "duck"). At low temperatures (0 and 25°), there are high values for the activation energy (7-8 kcal/mole) in both regions of hydrogenation of the $-CH=CH-$ bond. At high temperatures (from 25 to 50°), the temperature coefficient of hydrogenation of the $-CH=CH-$ bond is insignificant and the apparent activation energy diminishes to zero.

The apparent hydrogenolysis energy in the 25-40° temperature range is equal to 13950 cal/mole.

LITERATURE CITED

- [1] D. V. Sokolsky and A. I. Vyugova, Sci. Rep. Kazakh State Univ., 13, v. 2, 59 (1951).
- [2] D. V. Sokolsky and L. A. Buvaikina, J. Phys. Chem., 25, 495 (1951).
- [3] A. M. Rubinshtein and N. A. Pribytkova, Bull. Acad. Sci. USSR, Div. Chem. Sci., 5, 502 (1945).
- [4] S. Yu. Elovich and G. M. Zhabrova, Theoretical Bases of the Hydrogenation of Fats, Acad. Sci. USSR Press (1948).
- [5] D. V. Sokolsky and V. A. Druz, Proc. Acad. Sci. USSR, 73, 949 (1950).

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MERCAPTANS AND DISULFIDES AS CHAIN TRANSFER AGENTS

IN THE THERMAL POLYMERIZATION OF STYRENE

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In the chain polymerization of vinyl compounds, initiated by free radicals, along with the three basic reactions — the formation of active centers, the growth of chains and their inactivation — so-called chain transfer reactions often occur which lead to a more or less marked lowering in the molecular weight of the polymer obtained without lowering the over-all rate of the polymerization.

These reactions ordinarily proceed during the polymerization of vinyl compounds in the presence of organic solvents which contain hydrogen or halogen and proceed particularly readily in the presence of alkylmercaptans. The latter are often used in technology under the name of regulators or modifiers, since even insignificant additions of these substances to a monomer are capable of evoking marked change in the molecular weight and properties of the end products of the reaction.

In the process of chain transfer there usually occurs the breaking away by the growing chain $RM_n\cdot$ of an atom of halogen or hydrogen (X) or of regulator XY , with simultaneous formation of a new free radical $Y\cdot$, which, reacting with the monomer, yields the beginning of a new growing chain $YM_n\cdot$. Consequently, in spite of the frequent breaking off of chains, the reaction is not terminated and, as a result of the repeated transfer of chains, polymer molecules are formed, the ends of which are mostly saturated with X and Y radicals.

The kinetics of these reactions was studied for the first time by Kamensky and Medvedev [1] in the case of polymerization of vinylacetate in benzene solution and by Medvedev, Koritskaya and Alekseeva [2] in the case of polymerization of styrene in the presence of benzene, its homologs and cyclohexane.

On the other hand, Mayo [3] indicated that at a low polymerization the dependence $\frac{1}{P} = \frac{1}{P_0} + \frac{[S]}{[M]}$ applies, where p_0 and p are the degrees of polymerization of the polymer obtained in the absence of regulator, and at a molar ratio of regulator to monomer equal to $[S] / [M]$.

Consequently, quantities which are the reciprocals of the average extent of polymerization ($1/p$) of the polymer obtained, are linear functions of the ratio $[S]/[M]$ and depend on a certain constant C , which Mayo called the transfer constant of the chain, and is equal to the ratio of the rate constants of the reactions of transfer and of growth of the chains. Thus the constant C characterizes the degree of activity of the solvent as an agent of chain transfer.

This constant was determined by Mayo [4] for a number of hydrocarbons and their halogen derivatives, and it turned out that with increasing mobility of the hydrogen in the hydrocarbons, it increased, for example in progressing from benzene to fluorine (at 100°) from $1.84 \cdot 10^5$ to $1.24 \cdot 10^8$, i.e., by almost 700 times. At 100° , carbon tetrachloride proved to be 1000 times more active than benzene. As regards the mercaptans, the constants for only a few of them are given in the literature, specifically for 4-alkylmercaptans [5,6,8], 3-ethoxypropanthiol and the ethyl ester of thioglycolic acid [5]. Their magnitude (at 60°) reaches 3.8 for tertiary-butylmercaptan and 20.0 for primary alkylmercaptans, i.e., it exceeds the constant for benzene at 60° ($0.18 \cdot 10^{-5}$) by a million times.

The great activity of mercaptans can be explained by the greater mobility of the hydrogen of the SH groups in them, which, as a consequence of this, is readily torn off by the growing radicals with simultaneous formation of $RS\cdot$ radicals which initiate the growth of new chains. Consequently, the end products of polymerization in these cases are polymers of the composition $RS(C_6H_5)_nH$, which was confirmed by their analysis [7,9].

As regards information of chain transfer by disulfides, such information is still limited to the data of Snyder [7] on the polymerization of styrene in the presence of diisopropylxanthogendisulfide, which proved to be a rather strong chain transfer agent. However its chain transfer constant was not determined, any more than the chain transfer constants of other disulfides, although it can be assumed that, as a consequence of the instability of the S—S bond, the capacity to transfer chains by the following scheme should be more or less inherent in all of them:



The material published in the literature does not permit one to judge whether, to what extent and in which directions the nature of the radical in compounds of the RSH and RSSR type influences their activity in the process of chain transfer, i.e., on their capacity to enter into reaction with growing chains, with the formation of new free radicals.

Consequently, we synthesized a number of mercaptans and disulfides which contain various fatty, fatty-aromatic, aromatic and heterocyclic radicals and determined their chain transfer constants in the process of thermopolymerization of styrene at 100° in the absence of oxygen. The constants were determined by Mayo's method in the majority of cases (when their magnitude did not exceed 5.0), i.e., via the determination of the average molecular weights of the polymers obtained in the presence of various quantities of regulator at low polymerization. However, in the case of the highly active mercaptans, this method, as a consequence of the rapid consumption of mercaptan even in the initial stages of polymerization, did not yield correct results. Consequently in these cases we used (where this was possible) another method of determining the chain transfer constant, which was based on the determination of the quantity of polymer formed and of unreacted mercaptan remaining in the process of polymerization of styrene [8].

The results of these experiments are set forth in Tables 1 and 2, from which it is evident that the chain transfer constants of the compounds which were investigated vary within very wide limits, specifically from 0.0045 to 28.0.

It follows from Table 1, that all the primary alkylmercaptans and their derivatives which contain the CH_2SH group are characterized by great magnitudes of the constants of the order of 15.0 and more, and, thus, are powerful chain transfer agents, while the secondary octylmercaptan with $C = 3.2$ is considerably less active. A similar difference in activity between primary and tertiary mercaptans was found by Gregg, Aldermann and Mayo [5] in the case of the primary dodecylmercaptan ($C = 18.7$ at 60°) and tertiary-butylmercaptan ($C = 3.6$). Thus, the occurrence of the SH group in the middle of the chain markedly lowers the activity of the mercaptan. However, lengthening the chain hardly influences the degree of the activity of primary mercaptans, as the table shows. However, the introduction of the COOR group in the alpha position to the SH group considerably increases the activity of the mercaptan. This is evident in the case of the methyl ester of thioglycolic acid investigated by us ($C = 27.6$) and also from the data of the authors named above for the ethyl ester of the same acid ($C = 58$ at 60°).

We succeeded in determining the constant of thioglycolic acid itself ($C > 14$) only by a viscosimetric method and its true value must be at least twice as large as was observed for the ester of this acid. It is evident from this, that the carboxyl group, found in the alpha position to an SH group, increases the activity of the latter no less strongly than the COOCH_3 group.

TABLE 1

Chain Transfer Constants of Aliphatic and Aliphatic-Aromatic Mercaptans and Disulfides

R	RSH	RSSR
CH_3CH_2-	—	0.0045
$\text{CH}_3(\text{CH}_2)_2\text{CH}_2-$	15.4	0.0068
$\text{CH}_3(\text{CH}_2)_3\text{CH}_2-$	15.3	0.0104
$\text{CH}_3(\text{CH}_2)_4\text{CH}_2-$	15.1	—
$\text{CH}_3(\text{CH}_2)_6\text{CH}_2-$	14.7	0.024
$\text{CH}_3(\text{CH}_2)_7\text{CHCH}_3$	3.2	0.0104
$\text{C}_6\text{H}_5-\text{CH}_2-$	25.5	0.011
$p-\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2$	26.0	0.021
$\alpha-\text{C}_{10}\text{H}_7-\text{CH}_2-$	24.6	0.033
$-\text{CH}_2\text{COOH}$	$> 14.0 *$	0.20
$-\text{CH}_2\text{COOCH}_3$	27.6	0.10
$\text{CH}_3\text{CO}-$	$> 14.7 *$	—
$\text{C}_6\text{H}_5\text{CO}-$	$> 6.23 *$	0.11
$(\text{CH}_3)_2\text{OCHCSS}-$	—	$> 7.5 *$

* The constants were determined viscosimetrically and therefore are less than the true values.

Analogous considerations force us to assume that the constant of the thioacetic acid ($C > 14.7$) is actually considerably higher, i.e., that the $\text{CH}_3\text{CO}-$ group, directly bound to the SH group, also markedly activates the latter.

As regards the disulfides, as is evident from Table 1, they are a hundred and even a thousand times less active than the corresponding mercaptans. Thus, for example, in proceeding from n-butylmercaptan to dibutyl disulfide, the chain transfer constant is diminished by 2250 times. However, as the chain is elongated (from C_4 to C_{18}) the constants of the disulfides visibly increase (from 0.0045 to 0.024), as a consequence of which the difference in the degree of activity of mercaptans and disulfides is diminished.

A still greater increase in the activity of the disulfides is observed under the influence of the COOR group, as is evident in the case of the dithiodiglycolic acid ($C = 0.2$) and its ester ($C = 0.1$).

This is evidence that lengthening the chain, and also introduction into the chain of a carboxyl group in the alpha position, reduces the strength of the S-S bond in disulfides.

As regards the influence of the introduction of aromatic nuclei into alkylmercaptans and disulfides in the alpha position, as is evident from Table 1, in the mercaptans it is expressed as a 1.7 - 1.8-fold increase in the activity of the primary alkylmercaptans, but has little influence on the activity of the disulfides. For example, primary dihexyldisulfide and dibenzoyldisulfide hardly differ from each other in the magnitude of the constant. However, replacement of the phenyl group in the latter by the β -naphthyl group increases the constant to 0.03, evidently also as a consequence of weakening of the S-S bond.

Judging by the magnitude of the chain transfer constant, this bond is still more weakened in dibenzoyldisulfide which is analogous to benzoyl peroxide but in contrast to the latter, dibenzoyldisulfide hardly accelerates the polymerization of styrene at all.

Thus, although the bond between atoms of sulfur and dibenzoyldisulfide is somewhat weakened, it is nevertheless comparatively strong.

On the other hand, although diisopropyldixanthogendisulfide also has slight influence on the rate of polymerization of styrene, the constant found for it viscosimetrically is $C = 7.5$, which must actually be still larger and markedly differs in its exceptionally large magnitude from the constant of the other disulfides which, evidently, is to be explained by the presence in this disulfide of the very unstable grouping

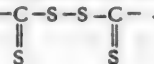
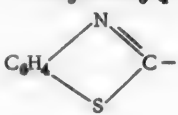
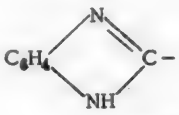


TABLE 2

Aromatic and Heterocyclic Mercaptans and Disulfides

R	RSH		RS-SR	
	% of the polymer	C	% of the polymer	C
$\text{C}_6\text{H}_5\text{--}$	7-12	0.08	3.7	0.14
$\text{--CH}_2\text{C}_6\text{H}_4\text{--}$	14-16	0.07	4.5	0.15
$\beta\text{-C}_{10}\text{H}_7\text{--}$	10	0.18	4.0	0.36
$\alpha\text{-C}_{10}\text{H}_7\text{--}$	9-16	0.15	4.2	1.57
$p\text{-C}_2\text{H}_5\text{OC}_6\text{H}_4\text{--}$	11-13	0.13	3.7	0.33
$o\text{-C}_2\text{H}_5\text{OC}_6\text{H}_4\text{--}$	3.5	25.1	4.2	0.075
$o\text{-HOCOC}_6\text{H}_4\text{--}$	3.5	<14.7	—	—
$o\text{-CH}_3\text{OCOC}_6\text{H}_4\text{--}$	3.0	17.0	4.0	0.20
	4.0	0.26	3.5	2.73
	4.3	0.21	—	—

In proceeding to the aromatic and heterocyclic mercaptans and disulfides, which are characterized by the presence of a direct bond of the sulfur atoms with the aromatic nuclei or heterocyclic rings, the marked difference of the constants of many representatives of these groups of compounds from those of the aliphatic and aliphatic-aromatic compounds should be noted.

The chain transfer constants of these compounds and the average polymer yields obtained in their presence are compared in Table 2.

The mercaptans of this type are characterized in the majority of cases by very low chain transfer constants, which vary from 0.07 to 0.26. Thus, in their activity they are 100-200 times less than the primary and 25-30 times less than the secondary and tertiary alkylmercaptans. This group includes thiophenol, thio-p-cresol, p-ethoxy-thiophenol and α - and β -thionaphthols and also 2-mercaptobenzthiazole and 2-mercaptobenzimidazole. At the same time it should be noted, that thiophenol and its para-substituted derivatives, and also thionaphthols, cause an increase in the yields of polystyrene from 3.5-4.0 to 7-16%, i.e., a 2-4-fold acceleration of the polymerization, possible as a consequence of their autooxidation with formation of peroxides [13,14]. However, the ortho-substituted derivatives of thiophenol, which contain oxygen as a substituent, such as, for example, o-ethoxythiophenol, thiosalicylic acid and its methyl ester, are distinguished by high constants of the order of 17.0-25.0, i.e., are not second to primary alkylmercaptans in their activity. However, in contrast to the thiophenols and their para-substituted derivatives, they are incapable of accelerating the polymerization of styrene.

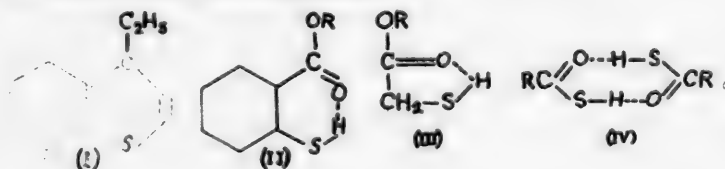
As regards the disulfides which correspond to the mercaptans indicated above, they all had comparatively high constants, the magnitude of which varied from 0.14 to 2.7, as a consequence of which the disulfides under consideration (with the exception of the ortho-substituted compounds) proved to be 2-10 times more active than the corresponding mercaptans.

The increasing activity of the aromatic disulfides, which rises from the phenyl derivatives through the β -naphthyl to the α -naphthyl and benzthiazolylic disulfides can be explained as a weakening of the S-S bond under the influence of unsaturated radicals adjacent to the sulfur atoms similarly to what is observed more clearly with the central C-C bond of hexaarylethanes, which undergoes rupture with formation of free radicals merely as a result of entering into solution. However, judging by the fact that these disulfides do not substantially change the rate of polymerization of styrene even at large chain transfer constants of the order of 2.0, the rupture of their S-S bond under the conditions of the polymerization is evidently accomplished only due to their reaction with the growing chains, and the $\text{ArS}\cdot$ radicals formed from them are sufficiently active to cause the formation of new chains.

The low activity of thiophenols, thionaphthols and heterocyclic mercaptans, is possibly associated with the presence in them of the $\text{C}=\text{C}-\text{SH}$ and $\text{N}=\text{C}-\text{SH}$ groups, which are distinguished by an increased acidity and a tendency to split off hydrogen in the form of a proton and not of an atom, as is required for the chain transfer mechanism. The increased activity of the aliphato-aromatic mercaptans of the ArCH_2SH type in comparison with alkylmercaptans can, on the contrary, be explained by the lowered degree of their acidity under the influence of aryl groups, since it is well known that replacement of the hydrogen of the CH_3 group by aryl groups increases the basic properties of the carbinol. The marked increase in the chain transfer constant in passing from thiophenol and its para-substituted derivatives to oxygen-containing ortho derivatives is, however, most unexpected.

In this connection, a particularly significant example is that of the isomeric ethoxythiophenols, of which the para-isomer is distinguished by a very low activity ($C = 0.13$), while the ortho-isomer, on the contrary, is remarkably active ($C = 25.4$). However, the high activity of other compounds which contain oxygen in positions 5 and 6 relative to the hydrogen of the SH group, for example, thiosalicylic and thioglycolic acids and their esters ($C = 17$ and 28) is also very significant.

The high activity of all these compounds, apparently, is caused by their cyclization due to the formation of intramolecular hydrogen bonds of the $\text{S}-\text{H} \cdots \text{O}$ type. The formation of hydrogen bonds in the case of oxygen analogs of these compounds, for example, salicylic acid and guaiacol, has long been known and demonstrated by various methods. As regards the mercaptans, their properties give no basis for assuming the presence in them of hydrogen bonds of the $\text{S}-\text{H} \cdots \text{S}$ type; these bonds can not arise in the given case due to the insufficient electronegativity of sulfur. However, there are data which indicate the possibility of the formation of intermolecular $\text{S}-\text{H} \cdots \text{O}$ bonds in solutions of mercaptans in ethers [15]. There are, therefore, grounds for assuming that such bonds arise within the molecules, in particular, if their formation leads to the formation of stable 5- and 6-membered rings. In particular, theory would lead one to expect the possibility of the formation of such rings in the case of the afore-mentioned o-ethoxythiophenol (I), thiosalicylic acid and its esters (II) and thioglycolic acid and its esters (III), and also does not exclude the possibility of the formation in the case of thioacetic and thiobenzoic acids of 8-membered rings of a type (IV), analogous to that which is assumed in the case of carboxylic acids. However, these assumptions require experimental confirmation and the problem of the activating influence of hydrogen bonds of the $\text{S}-\text{H} \cdots \text{O}$ type on the capacity of mercaptans to transfer chains is still unsettled.



EXPERIMENTAL

We prepared 22 mercaptans and 20 disulfides (Tables 1,2). They were all isolated in the pure form and had the constants indicated in the literature.

The initial styrene was subjected to careful purification, dried and vacuum distilled before use. On heating to 99° in sealed ampoules in the absence of air, it was 3.5% polymerized after 2 hours, i.e., the normal rate of polymerization [10] was detected which is indicated for the absence of inhibitors or accelerators.

To determine the chain transfer constants, precisely weighed samples of the mercaptan or disulfide were dissolved in 5 g of styrene in 10 to 20 ml ampoules of standard form which were washed, steamed and dried before the experiment. They had two inlet tubes in the upper portion — to charge the reagents and to connect the system with a vacuum. The first inlet tube was sealed after charging. To prevent the influence of oxygen, air was eliminated from the ampoule by carefully displacing it with nitrogen purified from oxygen and evacuating it to a vacuum of 2 mm, whereupon the styrene solution was congealed with dry ice. After repeating the operation of filling with nitrogen and evacuating for 3 or 4 times, the ampoules were sealed in a vacuum and heated in a thermostat and $99 \pm 0.5^\circ$ for 2 hours, after which they were quickly cooled with water and opened. With the object of determining the yield of polymer (it did not ordinarily exceed 5%) a sample was taken from the solution to find the coefficient of refraction. The content of polymer in the solution was calculated by the formula [8]: % polymer = $1.73 \cdot 10^3 \cdot \Delta n_D^{20}$, where Δn_D^{20} is the difference between the coefficient of refraction of the solution before and after polymerization. As the experiments showed, the yield of polymer determined in this way coincided with the yield found by weighing the polymer precipitated from methanol solution.

To determine the molecular weight of the polymers, the latter were precipitated from a solution of a 5-fold quantity of methanol and dried in a vacuum at 80° to constant weight. The specific viscosity of their benzene solutions was then determined at 20° at various polymer concentrations, and in all cases a linear dependence of the quantity η_{sp} / c on the concentration c was observed.

The characteristic viscosity $[\eta]$ was found by graphic extrapolation of the quantity η_{sp} / c to zero concentration. The average numerical molecular weight of the polymers was calculated by the formula $M_n = 184000 [\eta]^{1.4}$ introduced by Gregg and Mayo [11] for polystyrenes obtained in the polymerization of styrene in the presence of carbon tetrachloride at low percentages of conversion.

With the object of finding the chain transfer constants which characterize the sulfur compounds under study, the polymerization of styrene was carried out at 3 or 4 different concentrations of each compound, and depending on the degree of activity of the latter, the molar ratio of reagents $[XY] / [M]$ was varied within limits of from 0.0001 to 0.016 moles of the substance under investigation per mole of styrene.

The experiments showed that all the mercaptans and disulfides investigated by us to a greater or lesser extent lowered the average degree of polymerization (p) of the polystyrenes obtained in their presence, while the magnitudes of $1/p$ increased linearly in accord with the Mayo equation with increase in the ratio $[XY] / [M]$. This dependence is expressed by straight lines for various compounds which intersect at the point $1/p_0$, corresponding to the value of $1/p$ for pure styrene, but which have varying inclinations as a consequence of the varying degree of activity of the compounds taken.

The chain transfer constants (C) were calculated from these data by the Mayo formula, on the assumption that at an insignificant depth of polymerization the ratio of the reagents in the polymerization process remains practically constant. However, in the case of highly active mercaptans with $C \geq 5$, the constants obtained by this method, as a consequence of the rapid consumption of the mercaptan, remained considerably lower than the true values. In these cases the constants (C) of the mercaptans were also determined by us by titration of the amount of mercaptan which was not consumed in the polymerization at various degrees of conversion of the monomer into the polymer [8].

We accomplished the quantitative determination of mercaptans in the solution by the method of Kolthoff and Harris [12], i.e., by the amperometric titration of mercaptan with silver nitrate in the presence of ammonia. With this object the solution of the mercaptan in styrene was heated in sealed ampoules at 99° for various lengths of time, after which an exactly weighed sample of the polymerizate was diluted with methyl or ethyl alcohol, the polymer was filtered off and washed with alcohol, and the mercaptan was determined in the filtrate by the method indicated above.

The constants, found by this method, were calculated according to the formula:

$$C = \frac{2 - \log \% (\text{RSH})}{2 - \log \% (\text{M})}$$

where % (RSH) and % (M) are the quantities of unreacted substances (mercaptan and monomer), expressed in percentages of the initial quantities.

The experimental data, on the basis of which the average values indicated in Tables 1 and 2 for the chain transfer constants of the mercaptans and disulfides studied by us in the styrene polymerization process were calculated, are presented in Tables 3 and 4.

TABLE 3

Type of regulator		R-SH			R-S-S-R			
R	% RSH	Time (min.)	% of polymer	RSH remaining in % of the original	$\frac{[R_2S_2]}{[M]} \cdot 10^3$	% of polymer	$[\eta]$	$\frac{1}{P} \cdot 10^3$
$CH_3(CH_2)_3-$	0.29	60	1.56	78.2	4.16	3.5	1.904	0.229
		120	3.63	56.9	8.33	3.8	1.744	0.259
		180	5.00	45.2	16.7	3.8	1.536	0.310
$CH_3(CH_2)_5-$	0.38	60	2.25	70.1	4.16	4.0	1.772	0.254
		180	5.20	44.0	8.33	4.0	1.634	0.284
		240	6.92	34.0	16.7	4.3	1.376	0.362
$CH_3(CH_2)_8-$	0.42	35	1.73	76.8	4.16*	3.6	1.980	0.217
		240	7.27	33.2	8.33	3.5	1.884	0.233
		360	9.17	23.3	16.7	4.0	1.644	0.280
$CH_3(CH_2)_{17}-$	0.89	20	1.38	82.4	4.16	4.0	1.590	0.295
		120	3.63	56.2	8.33	4.5	1.280	0.400
		180	5.36	44.6	16.7	5.4	0.967	0.592
$CH_3(CH_2)_8CHCH_3$	0.46	120	3.46	90.2	4.16	3.5	1.762	0.256
		180	5.0	83.1	8.33	3.6	1.634	0.285
		240	6.9	82.1	16.7	3.8	1.368	0.365
CH_3OCOCH_2-	0.32	120	3.46	37.5	4.16	3.6	0.920	0.630
		180	5.19	23.2	8.33	3.8	0.626	1.090
		240	6.23	17.0	16.7	4.0	0.438	1.800
$C_6H_5CH_2-$	0.39	60	2.08	58.9	4.16	3.8	1.770	0.254
		180	5.71	22.2	8.33	3.8	1.604	0.292
		240	7.44	13.7	16.7	4.5	1.314	0.386
$p-CH_3OC_6H_4CH_2-$	0.46	60	1.21	70.5	2.08	4.1	1.770	0.254
		120	3.1	46.3	4.16	4.0	1.638	0.283
		180	5.2	25.6	8.33	4.5	1.360	0.368
$\alpha-C_{10}H_7CH_2-$	0.55	60	2.9	48.4	2.08	3.8	1.656	0.280
		120	7.6	14.2	4.16	3.6	1.444	0.340
		240	9.9	7.6	8.33	3.5	1.150	0.470
$o-C_2H_5OC_6H_4-$	0.62	60	2.4	55.0	2.08	3.8	1.360	0.367
		120	3.5	40.0	4.16	4.0	1.082	0.506
		180	5.4	24.4	8.33	4.5	0.775	0.808
$o-CH_3OCOC_6H_4-$		120	2.8	62.9	1.04	3.8	1.940	0.223
		180	4.15	49.3	2.08	4.5	1.826	0.243
		240	6.4	31.7	4.16	4.3	1.648	0.281

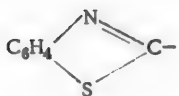
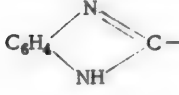
* $R=C_2H_5$

SUMMARY

1. The thermopolymerization of styrene at 99° in the presence of 22 mercaptans and 20 disulfides, belonging to the aliphatic, aromatic and heterocyclic series of compounds, was studied. The molecular weights of the polymers obtained at low levels of polymerization were determined, and quantitative data on the rate of disappearance of highly active mercaptans during the polymerization was also obtained.

2. The magnitudes of the chain transfer constants calculated from these data showed that not only mercaptans, but disulfides as well, can transfer chains, and that the degree of activity of either kind of compound is influenced by the structure of the radicals bound to the sulfur.

TABLE 4

Type of regulator	R-S-H				R-S-S-R			
R	[RSH] [M]	% of polymer	[η]	$\frac{1}{P} \cdot 10^3$	$\frac{[R_2S_2]}{[M]} \cdot 10^3$	% of polymer	[η]	$\frac{1}{P} \cdot 10^3$
C_6H_5-	2.08	7.1	1.354	0.370	2.08	3.6	1.062	0.52
	4.16	8.8	1.070	0.514	4.16	3.6	0.760	0.83
	8.33	12.1	0.748	0.849	8.33	3.8	1.536	1.35
$p-CH_3C_6H_4-$	0.00	3.4	2.074	0.200	2.08	4.1	1.062	0.52
	4.16	13.8	1.125	0.479	8.33	4.1	0.494	1.14
	8.33	15.6	0.770	0.815	12.5	5.0	0.388	2.13
$p-C_2H_5OC_6H_4-$	2.08	10.6	1.144	0.47	1.04	3.6	1.010	0.56
	4.16	13.0	0.820	0.74	2.08	3.6	0.723	0.89
	—	—	—	—	4.16	3.8	0.479	1.58
$\alpha-C_{10}H_7-$	2.08	8.7	1.112	0.49	0.52	3.8	0.646	1.04
	4.16	13.0	0.867	0.69	1.04	4.0	0.432	1.83
	8.33	16.1	0.700	0.93	2.08	4.7	0.273	3.48
$\beta-C_{10}H_7-$	2.08	10.4	0.946	0.61	0.416	3.6	1.340	0.375
	4.16	9.7	0.710	0.91	1.04	3.8	0.992	0.572
	—	—	—	—	4.16	4.3	0.475	0.603
	1.04	3.5	1.070	0.51	0.26	3.3	0.714	0.91
	2.08	3.5	0.829	0.74	0.52	3.8	0.470	1.63
	4.16	4.1	0.578	1.22	1.04	3.6	0.300	3.05
	0.104	4.3	1.941	0.223	0.52 *	3.8	0.220	4.71
	0.208	4.3	1.820	0.244	1.04	4.0	0.142	8.69
	—	—	—	—	2.08	5.2	0.095	15.26
C_6H_5CO-	0.104	3.8	0.720	0.89	1.04	3.8	1.514	0.32
	0.208	3.1	0.508	1.46	4.16	4.3	1.242	0.42
	0.416	3.8	0.361	2.35	8.33	4.0	0.614	1.12
$HOCOCH_2-$	0.104	3.6	0.430	1.84	0.42	3.6	1.564	0.30
	0.208	3.6	0.281	3.34	1.25	3.3	1.140	0.47
	0.416	3.6	0.190	5.78	2.08	3.5	0.950	0.61
$o-HOCOC_6H_4-$	0.104	3.6	0.434	1.82	0.104 **	3.6	0.462	1.67
	0.208	3.5	0.280	3.36	0.208	3.5	0.270	3.53
	0.416	3.5	0.183	6.09	0.416	3.6	0.184	6.05

* $R = (CH_3)_2CHOCs-$ ** The regulator was CH_3COSH

3. The introduction of aromatic radicals into the α -position to the SH group markedly increases the activity of the alkylmercaptans, but the direct linkage of this group with aromatic nuclei or heterocyclic rings leads to a marked reduction in the activity of the mercaptan.

4. A considerable increase in the constants is also observed upon the introduction of alkoxy or carboxylic groups into the α -position to the SH group in aliphatic mercaptans, and into the ortho-position to the SH group in thiophenols, which can be explained by the formation of intramolecular hydrogen bonds of the $S-H \cdots O$ type with the formation of 5- and 6-membered rings.

5. Dialkyldisulfides are distinguished by a low activity. Replacement of the alkyl groups by aromatic and heterocyclic radicals causes, however, a marked increase in the values of the chain transfer constants, as a consequence of which many aromatic disulfides display a greater activity than the corresponding thiophenols. Of the disulfides investigated, diisopropyldixanthogendisulfide proved to be exceptionally active.

LITERATURE CITED

- [1] S. Kamenskaya, S. S. Medvedev, J. Phys. Chem., 14, 922 (1940).
- [2] S. S. Medvedev, O. O. Koritskaya, E. N. Alekseeva, J. Phys. Chem., 17, 391 (1943).
- [3] F. R. Mayo, J. Am Chem. Soc., 65, 2324 (1943).
- [4] F. R. Mayo, J. Farad. Soc. (Disc.) 2, 328 (1947).
- [5] R. R. Gregg, D. M. Aldermann, F. R. Mayo, J. Am Chem. Soc., 70, 3740 (1948).
- [6] Ch. Walling, J. Am. Chem. Soc., 70, 2561 (1948).
- [7] H. P. Snyder, I. M. Steward, R. E. Allen, R. I. Dearborn, J. Am. Chem. Soc., 68, 1422 (1946).
- [8] N. V. Smith, J. Am. Chem. Soc., 68, 2059 (1946).
- [9] A. L. Klebansky, R. M. Sorokina, Trans. III Conf. on High Molecular Weight Compounds, Moscow - Leningrad, 10, (1948);
- [10] G. V. Schultz, E. Husemann, Z. phys. Chem., (B) 36, 184 (1937);
- [11] R. R. Gregg, F. R. Mayo, J. Am Chem. Soc., 70, 2373 (1948).
- [12] I. M. Kolthoff, W. E. Harris, Ind. Eng. Chem., An. Ed., 18, 161 (1946)
- [13] M. S. Kharasch, J. Am. Chem. Soc., 56, 717 (1934);
- [14] S. O. Jones, E. E. Reid, J. Am. Chem. Soc., 60, 2453 (1938).
- [15] W. Gordy, Stanford, J. Am. Chem. Soc., 62, 497 (1940).

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SYNTHESIS AND CONVERSION OF α - GLYCOLS OF THE ETHYLENIC SERIES. II

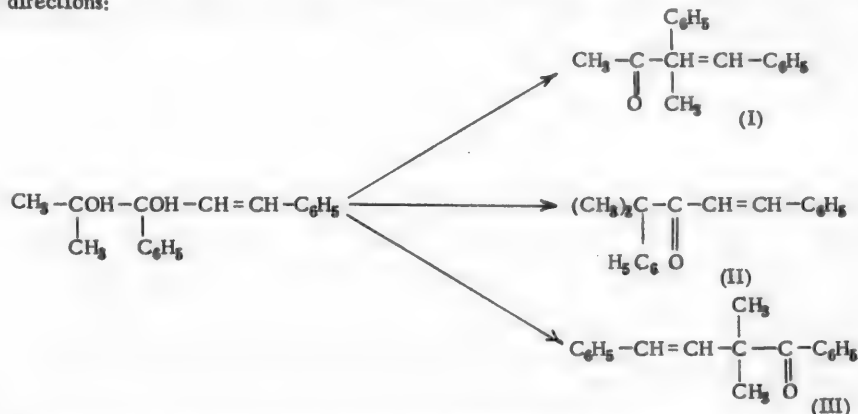
L. F. Chelpanova and V. A. Kormer

The investigation of the conversions of α -glycols (pinacols) of the ethylenic series under the influence of acidic catalysts is of interest not only as an attempt to fill the specific gap in the literature concerning the ethylenic α -glycols, but also as an opportunity to observe the manifold forms of conversions which are observed among the pinacols of the acetylenic series [1].

In the present work are described the conversions of the trans isomer of 2-methyl-2,5-diphenylpentene-4-diol-2,3 heated in the presence of 14 and 20 % alcoholic solutions of sulfuric acid. This glycol was obtained by the catalytic hydrogenation of the corresponding acetylenic glycol - 2-methyl-3,5-diphenylpentyn-4-diol-2,3 [2].

On heating the trans isomer of the ethylenic glycol (m.p. 85-86°) with a 14% alcoholic solution of H_2SO_4 to 55-60°, about 70% of the initial glycol (m.p. 85-86°) was recovered, as well as about 5% of a yellow-orange oily substance which was not investigated on account of the small yield; consequently, subsequent experiments were carried out with a 20% alcoholic solution of H_2SO_4 at 60-70°. Under these conditions 30% (calculating on the basis of the initial glycol) of a light yellow oily substance with a b.p. of 210° at 15 mm was isolated from the acidic solution. The substance had an empirical formula of $C_{18}H_{18}O$, gave a negative reaction for the hydroxyl group, and decolorized an aqueous solution of potassium permanganate and bromine water. Two isomeric dinitrophenylhydrazones with melting points of 68° and 172° were isolated as a result of the action on it of 2,4-dinitrophenylhydrazine (similar cases have been described in the literature [3]).

The formation of an unsaturated ketone is satisfactorily explained by the assumption that the glycol under investigation undergoes the pinacolic rearrangement in the presence of H_2SO_4 which is observed in ditertiary α -glycols under the influence of acidic catalysts. In the present case, the reaction can theoretically go in three directions:

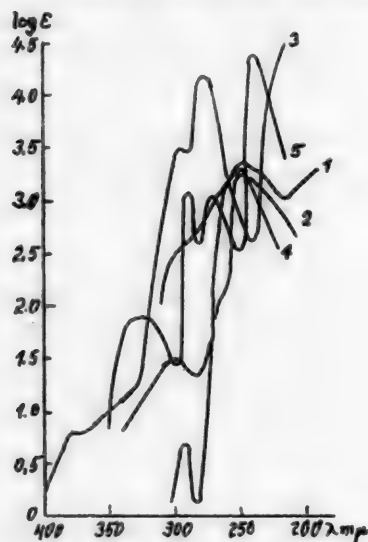


The structure of the unsaturated ketone was demonstrated by oxidation with an aqueous solution of potassium permanganate while the solution was heated. The oxidation products - acetophenone, acetic and benzoic acids - permit the structure of 3-methyl-3,5-diphenylpenten-4-one-2 (I) to be assigned to this substance. The oxidation data were confirmed by investigation of the absorption spectrum of the ketone in the infrared and ultraviolet regions.

In view of the theoretical possibility of obtaining three different unsaturated ketones, we compared the ultraviolet absorption curves of the following substances: the trans isomer of 2-methyl-3,5-diphenylpentene-4-diol-2,3, the trans isomer of 3-methyl-3,5-diphenylpenten-4-one-2, benzalacetone, syn -methyl-phenylethylene and propylphenylketone. * It is evident from the figure that the absorption curves of the ketone being investigated are

* The ultraviolet absorption spectra were recorded on a ISP-22 quartz spectrograph. An "Etalon" works hydrogen lamp served as the source of ultraviolet radiation with a continuous spectrum. A cuvette with a variable thickness and with a maximum layer thickness of 10 mm was used in taking the spectra. Hexane solutions of concentrations varying from 0.01 to 0.001 mole/ml were investigated. The method of equal blackening was used for the photomeasurements.

characterized by the presence of two bands with λ 2990 and 2500 Å. The curves of the initial glycol and the ketone being investigated have an identical kind of absorption with a maximum λ 2500 Å. We assumed that the absorption band with λ 2500 Å was caused by the presence in the initial glycol of the atomic grouping $-\text{CH}=\text{CH}-\text{C}_6\text{H}_5$; which is preserved in the transformation product. This is quite well confirmed by the absorption curve of $\text{CH}_3-\text{CH}=\text{CH}-\text{C}_6\text{H}_5$ which has one band with λ 2540 Å. The preservation of the absorption band with λ 2500 Å is caused by the presence of the atomic grouping $-\text{CH}=\text{CH}-\text{C}_6\text{H}_5$, which is possible in the ketone under investigation only when the latter is isolated from the carbonyl group. In the opposite case, as is evident from the absorption curve of benzalacetone, the band with λ 2500 Å does not appear.



1) Trans isomer of 2-methyl-3,5-diphenylpentene-4-diol-2,3; 2) trans isomer of 3-methyl-3,5-diphenylpentene-4-one-2; 3) benzalacetone; 4) sym.-methylphenyl ethylene; 5) propylphenylketone.

The absorption band in the ketone under investigation with λ 2990 Å characterizes the presence of the carbonyl group. The curve cited for the absorption of



excludes the presence in the ketone under investigation of the atomic grouping $(\text{C}_6\text{H}_5-\text{CO}-)$.

What has been set forth above completely confirms the data obtained during the oxidation, and permits the structure of 3-methyl-3,5-diphenylpentene-4-one-2 (I) to be assigned to the isomerization product; this is confirmed quite well by the available literature data, which refer to the great mobility of a hydroxyl group which stands in the α -position to an unsaturated bond [4].

EXPERIMENTAL

Preparation of 3-methyl-3,5-diphenylpentene-4-one-2 (I)

4 g of the trans isomer of 2-methyl-3,5-diphenylpentene-4-diol-2,3 with a m.p. of 85-86° was heated with a 20% alcoholic solution of H_2SO_4 [5 ml of H_2SO_4 (d 1.84) per 40 ml of $\text{C}_2\text{H}_5\text{OH}$ (96%)] for 5 hours at 60-70°. The mixture gradually assumed a yellow color which subsequently was converted into a cherry red color. Upon completion of the heating the mixture was diluted with 250 ml of cold water, and an ether extract was made. The acidic solution was neutralized after ether extraction with soda and did not contain any organic substances. This substance, obtained from the ethereal extract [after distillation under reduced pressure (210°, 15 mm)] consisted of a light yellow oil with a pleasant odor. The experiment was repeated with 30 g of the substance and gave analogous results:

d_4^{20} 1.0506; n_D^{20} 1.5782; M_R 79.00; Calc. 77.70

9.08 mg. sub.: 28.80 mg CO_2 ; 5.99 mg H_2O . 7.27 mg sub.: 23.04 mg CO_2 ; 4.77 mg H_2O . 0.2333 g sub.: 17.7 g benzene: Δt 0.26°. Found %: C 86.56, 86.49; H 7.38, 7.36; M 253.5. $\text{C}_{18}\text{H}_{18}\text{O}$: Calculated %: C 86.40; H 7.20; M 250.

The substance reacted with bromine water and with an aqueous solution of potassium permanganate, showed the absence of the hydroxyl group with Grignard reagent and the presence of the keto group with 2,4-dinitrophenylhydrazine. The 2,4-dinitrophenylhydrazones of the substance under investigation were obtained under the usual conditions [5]. In 5 minutes after mixing alcoholic solutions of the substance and 2,4-dinitrophenylhydrazine, a red precipitate settled out, which was filtered off and recrystallized from ethyl alcohol with a small addition of ethyl acetate.

On the following day after recrystallization, red crystals settled out. The mother liquor was left to stand. Toward the end of the day, light yellow crystals precipitated from it which were once more recrystallized from alcohol. The red crystals melted at 68-70°, the yellow, at 172-173°.

Investigation of the Dinitrophenylhydrazone with a M.P. of 68-70°.

4.01 mg sub.: 0.453 ml N₂ (22°, 765 mm). 3.38 mg sub.: 0.370 ml N₂ (19°, 775 mm). 7.02 mg sub.: 17.23 mg CO₂; 3.21 mg H₂O. Found %: N 13.16, 13.06; C 66.90; H 5.18. C₂₄H₂₂O₄N₄. Calculated %: N 13.02, C 67.00; H 5.11.

Investigation of the Dinitrophenylhydrazone with a M. P. of 172-173°.

5.74 mg sub.: 0.655 ml N₂ (20°, 760 mm). 4.77 mg sub.: 0.496 ml N₂ (20°, 761 mm). Found %: N 12.89, 12.95. C₂₄H₂₂O₄N₄. Calculated %: N 13.02.

The two hydrazones with different melting points were, apparently geometrical isomers. Upon heating the red isomer (m.p. 68-70°) above its melting point it was converted into the yellow isomer with a m.p. of 172-173°. Both hydrazones gave a negative pyrazoline reaction.

Oxidation of the ketone

An acetophenone, which gave a 2,4-dinitrophenylhydrazone with a m.p. of 237°, was isolated by oxidation with an aqueous solution of potassium permanganate (1.5 g ketone; 0.9 g KMnO₄; 60-70°) and by the usual separation of the neutral and acidic oxidation products from the neutral substances. The aqueous solution of the acidic products contained benzoic acid with a m.p. of 122.0°, which was characterized by a mixed melting point test, and acetic acid, characterized by analysis of the silver salt.

0.0535 g sub.: 0.0582 g CO₂; 0.0156 g H₂O. Found %: C 14.57; H 1.61; Ag 65.01. CH₃COOAg

Calculated %: C 14.45; H 1.81; Ag 64.67.

SUMMARY

Upon the dehydration of 2-methyl-3,5-diphenylpentene-4-diol-2,3 under the influence of a 20% alcoholic solution of H₂SO₄, a pinacolic rearrangement occurs, as a result of which 3-methyl-3,5-diphenylpenten-4-one-2, which has not been described in the literature, is formed. Two 2,4-dinitrophenylhydrazones of this ketone with m.p. of 68-70 and 172-173° were obtained.

LITERATURE CITED

- [1] E. D. Venus-Danilova, E. P. Brichko, L. A. Pavlova, J. Gen. Chem., 19, 951 (1949).*
- [2] L. F. Chelpanova and Z. V. Printseva, J. Gen. Chem., 23, 1135 (1953). **
- [3] I. N. Nazarov and S. S. Bakhmutskaya, J. Gen. Chem., 20, 1835 (1950).***
- [4] A. E. Favorsky and A. S. Onishchenko, J. Gen. Chem., 11, 1113 (1941); T. A. Favorskaya and A. N. Shirshova, J. Gen. Chem., 19, 177 (1949);****I. N. Nazarov and I. V. Torgov, J. Gen. Chem., 18, 1480 (1948).
- [5] R. Shriner and R. Fuson, Systematic Qualitative Analysis of Organic Compounds, p. 173 (1950).

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* See Consultants Bureau Translation, p. 941.

** " " " " p. 1189.

*** " " " " p. 1903.

**** " " " " p. 159.



CONFIGURATION AND PROPERTIES OF UNSATURATED ACIDS AND THEIR DERIVATIVES

II. PROPERTIES OF CINNAMIC ACIDS AND THEIR ESTERS

A. K. Plisov and A. I. Bykovets

We have shown in preceding communications [1] that the influence of radicals at the double bond is manifested differently in the *cis* and *trans* forms of such unsaturated acids as oleic and petroselinic acids and their esters. In addition, it was established that the *cis* and *trans* forms of the esters of these acids act differently in reactions, associated with their ester group; at the same time, the magnitude and structure of the alcohol radical had a definite influence.

These facts impelled us to set up experiments to elucidate and compare the reactivity of the cinnamic acids and their esters. It was necessary to elucidate the influence on the reactivity of these compounds of a phenyl and carboxyl or ester group, directly linked to the carbon atoms which were joined to the double bond.

The results of the experiments set up for this purpose are in excellent agreement with the data of our earlier experiments on other materials. In this case, too, it can be said that the *cis* and *trans* forms of the cinnamic acids (or their derivatives) are identically reactive both in relation to reactions at the double bond, and in relation to reactions associated with the ester group. In other words, the cinnamic acids and their esters manifest chemical activity in accordance with the theory of steric hindrance. Actually, *trans*-cinnamic acid with a m.p. of 133° is oxidized and hydrogenated considerably more slowly than the *cis* acid.

It is necessary to assume that the phenyl group, which is located on one side of the double bond, and the carbonyl and ester groups which are located on the other, hamper the access of the reagent to the double bond. In the *cis* form, in which both groups are found on only one side of the double bond, this influence is exerted to a lesser extent.

As regards saponification of the propyl esters of the cinnamic acids, the opposite picture is observed here, as one was bound to expect. The propyl ester of *trans*-cinnamic acid is saponified more quickly than the ester of *cis*-cinnamic acid.

Thus, in the present case, the ester group manifests its chemical activity differently in the *cis* and *trans* forms of the esters of the cinnamic acids.

It was necessary to obtain the difficultly-accessible *cis*-cinnamic acid for the study of these questions. The best way of preparing it was by isomerizing *trans*-cinnamic acid under the influence of ultraviolet light; under these conditions, as is well known, various forms of *cis*-cinnamic acid are obtained; most frequently we obtained one with a m.p. of 42° and another with a m.p. of 58°.

Up to the present time the opinion has been held that the three well-known forms of cinnamic acid with m.p. of 42, 58, and 68° are different crystalline modifications of the same acid, the molecules of which can be grouped in three ways in the crystals. However, if the results of our experiments involving the hydrogenation and oxidation of the cinnamic acids with m.p. of 42 and 58° are taken into account, it is impossible to agree with this. We firmly established that the two mentioned forms of *cis*-cinnamic acid are hydrogenated and oxidized in suitable solvents at an identical rate. Consequently, the question is not of the influence of crystalline forms on the reactivity, but of the different spatial configuration of the two forms of this acid. There is no sufficiently clear-cut information regarding this in the literature. It is possible that, in the present case, we have to do with a very rare phenomenon, associated with the limiting of the free rotation of the phenyl group in *cis*-cinnamic acid. The latter may be caused by the formation of hydrogen bonds between the phenyl and carbonyl groups. If we admit the possibility of three-dimensional, but not of plane distribution of the six carbon atoms of the benzene nucleus, then, probably, this can be explained by the presence of four forms of *cis*-cinnamic acid (allocinnamic acid). The three *cis*-cinnamic acids mentioned above are usually cited in the literature, but in fact, an additional, fourth acid with a m.p. of 36°, described by Erlenmeyer - Jr. [2] is also known. This form of *cis*-cinnamic acid has not been sufficiently studied, and is not usually mentioned in the current literature.

EXPERIMENTAL

Preparation of the Cinnamic Acids and their Propyl Esters

Commercial *trans*-cinnamic acid with a m.p. of 133° was used in the work. *Cis*-cinnamic acid was prepared by us, starting from the *trans*-cinnamic acid, via irradiation with ultraviolet light for 100 hours, of its benzene solution, placed in a quartz flask. After separating the mixture of acids obtained with the aid of the aniline salts and appropriate purification, in some cases predominantly *cis*-cinnamic acid with a m.p. of 42°, and in other cases, the isomer which melted at 58°, was obtained. The conditions for obtaining these isomers have been described in greater detail in the article by Stoermer [3].

The propyl ester of *trans*-cinnamic acid was prepared by the usual esterification reaction via heating *trans*-cinnamic acid with propyl alcohol in the presence of concentrated sulfuric acid. After purification, the ester had a b.p. of 283° and n_D^{25} 1.409.

The propyl ester of *cis*-cinnamic acid, still not described in the literature, was prepared from the silver salt of *cis*-cinnamic acid with a m.p. of 58° and propyl bromide. The propyl ester of *cis*-cinnamic acid was a colorless liquid with a pleasant, flower-like odor and a m.p. of 122-124° (at 15 mm); n_D^{20} 1.4244. The ester was quite soluble in alcohol, acetic acid and benzene.

Hydrogenation of the Cinnamic Acids

Equal samples of the cinnamic acids were placed in identical hydrogenation vessels ("goose vessels") for the hydrogenation. To weighed samples of about 0.5 g, the calculated quantity of soda solution was added and palladium catalyst, precipitated on BaSO_4 (0.05 g of the catalyst contained 0.001 g of Pd) was introduced. The vessels with the samples were placed in a shaking apparatus, and purified hydrogen was simultaneously passed in at low pressure in an appropriate manner.

The results of the hydrogenation of the cinnamic acids are presented on Fig. 1. There is a notable difference between the quantities of hydrogen added not only to the *cis* and to the *trans* forms, but even to the *cis*-cinnamic acids with differing melting points.



Fig. 1. Hydrogenation of the cinnamic acids. 1) *Cis*-cinnamic acid with a m. p. of 58°; 2) *cis*-cinnamic acid with a m.p. of 42°; 3) *trans*-cinnamic acid with a m.p. of 133°.

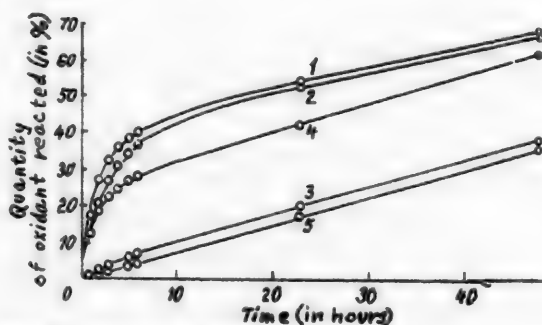


Fig. 2. Oxidation of the cinnamic acids.

1) and 4) *Cis*-cinnamic acid with a m.p. of 58°; 2) *cis*-cinnamic acid with a m.p. of 42°; 3) and 5) *trans*-cinnamic acid.

1), 2) and 3) at a temperature of 23°; 4) and 5) at a temperature of 15°.

Oxidation of the Cinnamic Acids and their Esters

Various oxidizing agents were tested in the study of the oxidation of cinnamic acids: KMnO_4 in acetone and aqueous solutions, $\text{K}_2\text{Cr}_2\text{O}_7$ in acetic acid solution, hydrogen peroxide, benzoyl peroxide and perbenzoic acid. Some of them (KMnO_4 and H_2O_2) proved unsuitable as a consequence of the fact that the oxidation with these oxidants proceeded with great speed, while others—benzoyl peroxide and perbenzoic acid—did not react at all. The result of these experiments was that $\text{K}_2\text{Cr}_2\text{O}_7$, dissolved in glacial acetic acid, proved usable for observations on the rate of oxidation.

Equimolecular quantities of 0.1 N $K_2Cr_2O_7$ solution in glacial acetic acid were added in our experiments to two identical samples of the acids or their esters, dissolved in acetic acid. Each of the forms of cinnamic acid was converted into benzaldehyde as a result of the oxidation.

Curves which characterize the relative rates of oxidation of cinnamic acids and their propyl esters at temperatures of 15° and 23° are presented in Figs. 2 and 3. The great difference between the relative rates of oxidation of the cis and trans acids and of their esters is also noticeable here. The esters are oxidized considerably more slowly than the corresponding acids. It is very important to note that oxidation of cinnamic acids with m.p. 42 and 58° proceeds at rates which are not identical; the acid with m.p. 42° is oxidized somewhat more slowly than its isomer with a m.p. of 58°.

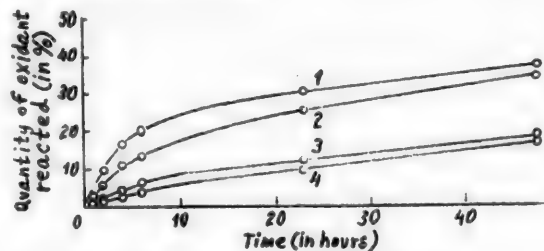


Fig. 3. Oxidation of the propyl esters of the cinnamic acids.

1) and 2) The propyl ester of cis-cinnamic acid;
3) and 4) the propyl ester of trans-cinnamic acid.
1) and 3) at a temperature of 23°; 2) and 4) at a temperature of 15°.

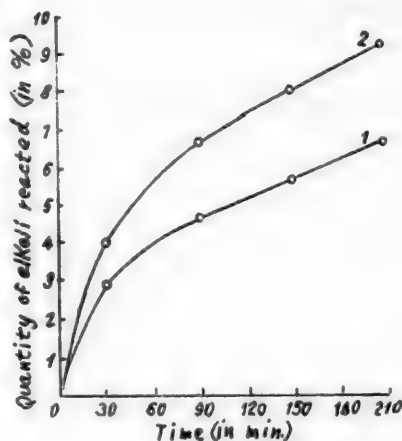


Fig. 4. Saponification of the propyl esters of the cinnamic acids. 1) The propyl esters of cis-cinnamic acid; 2) the propyl esters of trans-cinnamic acid.

Saponification of the Propyl Esters of the Cinnamic Acids

Identical samples of the esters, dissolved in anhydrous alcohol, were subjected to saponification with alcoholic alkali under identical conditions. The saponification was carried out with a 0.1 N solution of alkali at 20°. The alkali was taken in an equimolecular quantity in relation to the amount of the ester sample. 5 ml samples of the reaction mixture were taken at regular intervals from the small flasks, which were placed in a thermostat. The quantity of unreacted alkali in each sample was determined.

The change in the quantity of alkali with time during the saponification of the propyl esters of the cinnamic acids is shown in Fig. 4. The ester of trans-cinnamic acid is saponified more rapidly than the ester of the cis acid.

SUMMARY

1. The propyl ester of cis-cinnamic acid was synthesized and its properties were described.
2. A difference in the relative rates of hydrogenation of the cis- and trans-cinnamic acids was established: cis-cinnamic acid adds hydrogen more readily.
3. The oxidation of the cinnamic acids and their esters proceeds at varying rates. Cis-cinnamic acid and its ester are oxidized more quickly than trans-cinnamic acid and its ester; the esters are oxidized more slowly than the corresponding acids.
4. The saponification of the propyl ester of cis-cinnamic acid proceeds more slowly than saponification of this ester of trans-cinnamic acid.
5. It was established that the so-called "crystalline modifications" of cis-cinnamic acid (allocinnamic acid) with a m.p. of 42 and 58° have varying reactivities: cis-cinnamic acid with a m.p. of 42° is hydrogenated and oxidized more slowly than its isomer with a m.p. of 58°.

6. A hypothesis concerning the configuration of the cis form of the cinnamic acids was proposed.

LITERATURE CITED

- [1] A. K. Plisov and E. G. Maleeva, J. Gen. Chem., 23, 72 (1953);* A. K. Plisov and A. I. Bykovets, J. Gen. Chem., 23, 613 (1953),**
- [2] E. Erlenmeyer Jr., Ber., 37, 3361 (1904).
- [3] R. Stoermer, Ber., 44, 667 (1911).

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* See Consultants Bureau Translation, p. 69.
** " " " " " p. 637.

CONVERSION AND SYNTHESIS OF CARBOHYDRATES

XI. INVESTIGATION IN THE FIELD OF KETOSE OXIDATION

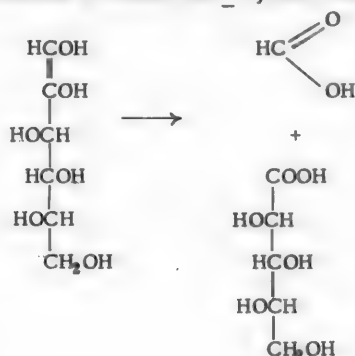
V. M. Berezovsky and L. I. Strelchunas

In one of the preceding communications [1], one of us studied the cleavage oxidation of aldose by oxygen in an alkaline medium [2]. It was found that the formation of d-arabonic acid by the oxidation of d-glucose proceeds only in a narrow temperature range between 40 and 50°; at a temperature above 50°, another reaction-route predominates, and at a temperature below 40° the rate of the reaction becomes too small for the oxidation reaction to be used for preparative purposes.

It was of interest to study the cleavage oxidation of ketose, in particular, the oxidation of 1-sorbose by oxygen in an alkaline medium [3], which proceeds with the formation of 1-xylonic acid. We showed that the oxidation reaction is accompanied by the absorption of 2 oxygen atoms and the splitting off of 1 carbon atom in the form of formic acid. The formation of 1-xylonic acid in a yield of 37% proceeds in the temperature range 24-42°; at a temperature above 42°, another reaction-route begins to predominate, while the oxygen requirement of 2 atoms of oxygen per molecule of ketose is the same, and at a temperature below 24°, the rate of the reaction becomes insignificant.

The circumstance that, in the oxidation of ketohexose by oxygen in an alkaline medium, 2 atoms of oxygen are absorbed, furnishes a basis for assuming that the formation of 1-xylonic acid from sorbose can not proceed via the intermediate formation and subsequent oxidation of 2-keto-1-gulonic acid, since in this case no less than 3 oxygen atoms would be required (in accord with the data on the oxidation of 2-keto-1-gulonic acid by hydrogen peroxide with 2 atoms of oxygen [4]). The absence of 2-keto-1-gulonic acid in the reaction described by us was established by a negative test for the formation of ascorbic acid.

The cleavage of 1 carbon atom with the formation of formic acid and the formation of pentonic acids in the oxidation of ketohexose by oxygen in an alkaline medium gives a basis for assuming that the mechanism of this reaction is of the same kind as the mechanism of the oxidation of aldohexose under the same conditions. The probable mechanism of the reaction of cleavage oxidation of sorbose by oxygen in an alkaline medium consists in an initial tautomeric conversion of the noncyclic form of 1-sorbose into the endiol form with an unsaturated bond between the first and second carbon atoms, which then undergoes oxidation by molecular oxygen with rupture of ethylenic bond and formation of formic and 1-xylonic acids:



Side reactions can proceed due to enolization at the second and third carbon atoms and, further, with migration of the double bond, at the third and fourth carbon atoms and so forth; in this case the oxidation reaction will be accompanied by the formation of glycolic and tetrionic acids and other oxidation products.

1-Xylonic acid was isolated from the oxidized solution in the form of the double cadmium salt with cadmium bromide; if the volatile organic acids and excess quantity of mineral salts are not preliminarily eliminated from the solution, then the isolation of the double salt of cadmium xylonate from the solution is made difficult.

The rate constant of the reaction of sorbose oxidation at 40° is $K = 0.05446$ as against $K = 0.01161$ for the glucose oxidation reaction at the same temperature. Thus, a considerably higher reactivity can be established

for ketose in comparison with aldoses (approximately 4.7 times greater) as regards the oxidation with oxygen in an alkaline medium. The increased reactivity of ketose is in complete accord with well known facts, for example, the predominant condensation of the keto groups of reductone (the enol of hydroxymalonic aldehyde) with the maximally reactive amino group in position 5 in 2,4,5-triamino-6-hydroxypyrimidine [5].

The formation of a small quantity of oxalic acid (about 0.8% of the theoretical) is observed in the cleavage oxidation of 1-sorbose by oxygen in alkaline medium, along with the formation of 1-xylonic acid. A similar type of side reaction was previously observed for the oxidation of aldose [1].

The method of single-stage preparation of 1-xylonic acid by cleavage oxidation of 1-sorbose presents considerable advantages in comparison with the two-stage method of oxidizing 1-sorbose, which proceeds in a sodium bicarbonate solution by the action of atmospheric oxygen in the presence of palladium catalyst, initially with formation of 2-keto-1-gulonic acid, and then with its subsequent oxidation by hydrogen peroxide.

EXPERIMENTAL

Cadmium 1-xylionate-cadmium bromide.

73 g of 1-sorbose, 60 g of potassium hydroxide in a solution (or an equivalent quantity of sodium hydroxide) and water to a volume of 560 ml were introduced into a rotating autoclave, filled with metallic gauze. The sorbose was oxidized with oxygen at 30-35° for 3 hours at an initial pressure of 30-35 atm.; 1 mole of oxygen was absorbed per mole of ketose. Upon completion of the oxidation, less than 0.5% of unchanged sorbose remained.

The oxidized solution was neutralized with hydrochloric acid (d 1.19, 70-80 ml) to a violet coloration with congo red and was concentrated in a vacuum. Water was added to the partially crystallized syrupy residue and it was again concentrated in a vacuum; this process was repeated 3-4 times, until the almost complete elimination of the volatile organic acids. The mineral salts were then filtered off, washed with ice water and 1-xylonic acid was isolated from the filtrate in the form of difficultly soluble double cadmium salt with cadmium bromide. For this purpose, 150 ml of water and, gradually, while heating to boiling, 35 g of cadmium carbonate, were added to the filtrate; upon completion of the evolution of carbon dioxide, the solution was filtered and 55 g of cadmium bromide was added to it. After crystallization 32.4 g (22%) of the double salt of cadmium xylionate was obtained in the course of several days.

The substance was recrystallized from a 15-fold quantity of water for analysis.

Found %: Cd 29.70. $C_{10}H_{18}O_{12}Br_2Cd_2 \cdot 2H_2O$. Calculated %: Cd 29.95.

Kinetics of the oxidation of 1-sorbose.

The study of the cleavage oxidation reaction of sorbose with oxygen in an alkaline medium was carried out in a glass column with sealed-in porous plates, 4 cm in diameter; the apparatus used has been described previously [1].

230 ml of aqueous solution, containing 36.5 g of 1-sorbose, was added to the column, and at a temperature several degrees below the assigned temperature, the passage of oxygen was initiated, after which 50 ml of a 40% solution of sodium hydroxide was added. The reaction was initially accompanied by the evolution of heat. After the solutions were mixed, the temperature of the mixture rose and remained constant throughout the entire duration of the experiment to within $\pm 0.2^\circ$. The oxygen was passed for as long as was necessary for the oxidation of no less than 95% of the sorbose (determined by analysis of the reducing substance). Upon completion of the oxidation reaction, the colorless solution obtained was treated in the way described above with the object of isolating the xylonic acid from it.

Since the reaction proceeds chiefly in a fine film (and to a lesser extent due to solution of the gas in the liquid), the oxygen was passed at a rate of 1.2 liter/minute (0.32-0.38 liter/minute per cm^2 of the surface of the Schott No. 3 plate), which corresponded to its optimal dispersion in the liquid and to the creation of a maximum contact surface of the liquid and gaseous phases. By diminishing the rate of passage of oxygen to 0.5 liter/minute, the surface of the film was diminished, which was accompanied by a diminution in the rate of the reaction.

The temperature factor has great influence not only on the rate of the oxidation of sorbose by oxygen in an alkaline medium, but also on the direction of the reaction. The results of experiments at variable temperature, conducted under conditions which created a maximum surface film with other conditions constant, are depicted in Fig. 1.

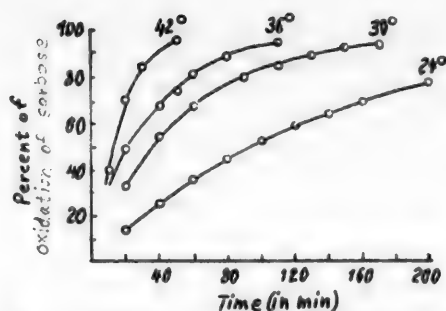


Fig. 1. Influence of temperature on the rate of the oxidation of sorbose by oxygen in an alkaline solution.

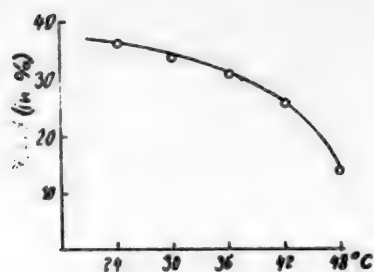


Fig. 2. Dependence of the yield of the complex salt of cadmium xylonate on the temperature.

At 24°, 25% of the sorbose undergoes oxidation in the first 40 minutes, while more than 6 hours is required for the oxidation of 95%. At 30°, 54% of the sorbose is oxidized in the first 40 minutes and 3 hours are necessary for 95% oxidation; at 36°, 68% of the sorbose is oxidized in the first 40 minutes and 95% in 1 hour and 45 minutes; at 42°, 95% of the sorbose is oxidized in the first 49 minutes.

Upon raising the reaction temperature above 36°, the yield of xylonic acid is markedly diminished with the simultaneous complete oxidation of the initial sorbose; the optimal temperature lies in the 24-36° range. The yields of xylonic acid depending on the oxidation reaction temperature (the yield is lowered from 36.4% to 13.6% when the temperature is raised from 24° to 48°) are presented in Fig. 2.

The rate constant of the cleavage oxidation of sorbose with oxygen was determined by us in an apparatus with a Schott No. 3 filter, 4 cm in diameter, with an optimal quantity of oxygen being passed (1.2 liter/minute); the temperature variation was within limits of $\pm 0.1^\circ$.

The rate constants of the reaction, which was determined by us to be monomolecular, were

$$K_{(24^\circ) \text{ av.}} = 0.00747; \quad K_{(30^\circ) \text{ av.}} = 0.01840;$$

$$K_{(40^\circ) \text{ av.}} = 0.05401.$$

The deviations of the values of the rate constants of the reaction from the average amounted to from 2 to 3.2%. The satisfactory constancy of K_{av} showed the monomolecular character of the cleavage oxidation of sorbose by oxygen in alkaline medium. The reaction is complex as regards the variety of products obtainable; however, the reaction of monoses with oxygen proceeds in strictly equimolecular ratios. Of the two reacting molecules—sorbose and oxygen—the variable quantity is the sorbose concentration; the quantity of oxygen is stable and excess.

Just as in the oxidation of glucose [1], there is an induction period for the oxidation reaction of sorbose of up to 15 minutes, in which period the rate constant of the reaction differs from its average value.

The temperature coefficient of the rate of the reaction amounts for temperatures of 30 and 40° to:

$$\frac{K_{(40^\circ)}}{K_{(30^\circ)}} = 2.93.$$

The activation energy, calculated by the Arrhenius equation on the basis of the rate constants of the reaction for 30 and 40°, amounts to $A = 20300$ calories.

Determination of oxalic acid

After the oxidation of 36.5 g of sorbose, we found from 0.462 to 0.463 g of oxalic acid in the solution. The quantity of oxalic acid is independent of the temperature conditions under which the reaction is conducted and of other variable factors. The determination was carried out by isolating oxalic acid from the neutralized solution in the form of its calcium salt with subsequent titration with potassium permanganate [1].

Determination of formic acid

An 0.1 portion of the solution,* after oxidation of 36.5 g of sorbose, was acidified with sulfuric acid solution and the excess mineral acid was then bound with potassium ammonium tartrate. We steam distilled off the formic acid from the solution obtained and trapped it with a solution of calcium carbonate in water; the volatile non-acidic compounds were eliminated from the receiving flask by steam distillation. After separating the precipitate, the content of formic acid in the filtrate was determined oxidimetrically. From 7.8 to 8.4 g of formic acid was found in the solution after oxidizing 36.4 g of sorbose; this amounted to 0.84-0.90 moles per 1 mole of sorbose, and did not depend on the yield of xylonic acid or on the temperature conditions under which the reaction was conducted.

Determination of 2-ketogulonic acid

10 ml of the solution after the oxidation of the sorbose was neutralized with hydrochloric acid (about 1 ml), 10 ml of hydrochloric acid (d 1.19) was added to the mixture and was heated with a reflux condenser for 90 minutes. Titration with potassium iodate demonstrated the absence of ascorbic acid and, consequently, the absence of 2-ketogulonic acid in the solution under investigation.

A control experiment with the addition to the solution under investigation of 0.160 g of known 2-ketogulonic acid and with the analysis conducted in the manner indicated above, demonstrated the presence of 0.107 g of ascorbic acid (i.e., 0.53% in the solution), which indicates that the precision of the method used was sufficiently great.

SUMMARY

1. The kinetics of the cleavage oxidation of l-sorbose by oxygen in alkaline medium was studied. In alkaline medium, ketoses react with oxygen in a strictly equimolecular ratio.
2. It was shown that ketoses have a considerably greater reactivity (approximately 4.7 times greater) than aldoses, as regards oxidation by oxygen.
3. It was shown that the oxidation of sorbose with the formation of xylonic acid proceeds in a narrow temperature range—at a temperature above 42°, another reaction route predominates.
4. The formation of oxalic acid as one of the side products of the reaction was established.

LITERATURE CITED

- [1] V. Berezovsky, J. Gen. Chem., Supp. II, 944 (1953).
- [2] O. Spengler, A. Pfannenstiel, Z. Wirtschaftsgruppe Zuckerind., 85, 546 (1935).
- [3] H. Isbel, J. Research Nat. Bur. Standards, 29, 227 (1942).
- [4] V. Berezovsky, E. Rodionova, L. Strelchunas, J. Gen. Chem., 24, 631 (1954).
- [5] V. Berezovsky, Prog. Chem., 22, 191 (1953).

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* Unit of measurement omitted in original text.—Publisher.

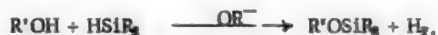
RECIPROCAL REACTION OF TRIALKYLSILANES WITH MONOCARBOXYLIC ACIDS.

A NEW METHOD OF SYNTHESIZING TRIALKYLACYLOXYSILANES

AND THEIR PHYSICAL PROPERTIES

B. N. Dolgov, N. P. Kharitonov and M. G. Voronkov

The present work is a continuation of our investigations devoted to the study of the reaction of the Si-H bond in silicoorganic compounds. We have previously studied [1] the reaction of trialkylsilanes with alcohols which is catalyzed by alcoholates of the alkali metals and which leads to the formation of trialkylalkoxysilanes in a yield of 80 - 90% of the theoretical:



The possibility of replacing the hydrogen atom bound to the silicon atom with a primary, secondary or tertiary alkoxy group was demonstrated as a result of the investigation.

Working out a method of replacing the hydrogen atom attached to the silicon atom with an acyloxy group by an analogous scheme was an additional goal of our work:



There are certain indications in the literature regarding the possibility of such substitution [2-4]. Reilly and Post [2], for example, observed the conversion of the Si-H bond into the Si-OCOCH₃ bond in the reaction of trialkoxysilanes with acetic anhydride:



Kautsky and Hirsch [3] indicate that acyloxy derivatives of siloxene are formed as a result of its reaction at the Si-H bond with carboxylic acids which can be represented by the scheme:



Acid anhydrides react analogously:



However, no one has tried to use these reactions for the preparative formation of silicoorganic esters of carboxylic acids. Up to the present time, these compounds have been obtained by the reaction of halogensilanes by organic acids [5-10], their salts [11-16], anhydrides [5], or esters [17], and also by the action of acid anhydrides on alkoxy substituted silanes [2, 16, 18-22] and amino substituted silanes [16]. The yields of acyloxy derivatives as a result of the indicated methods of synthesizing them rarely exceeds 50%. Trialkylacyloxysilanes can be prepared by the reaction of trialkylsilanes with acid chlorides [23] or anhydrides [24]. The synthesis of tetra-acyloxysilanes by the reaction of organic acids with SiS₂ [25] has also been described.

It has been shown, in the case of trialkylsilanes, in the present work that replacement of the hydrogen atom bound to the silicon atom by an acyloxy group can be readily accomplished by catalytic reaction with carboxylic acids or by reaction with mercury salts of organic acids, which proceeds according to the scheme:



The reaction of trialkylsilanes with organic acids is catalyzed by strong mineral acids (H₂SO₄ and HI) or by iodine. However, the best results were obtained by using a powdered mixture of aluminum and iodine, taken in a molar ratio 1:3:2 as the catalyst. The molar ratio of aluminum to the initial trialkylsilane amounted to 3.7% in all the experiments.

The reaction of trialkylsilanes with monocarboxylic acids was accomplished by heating to boiling a mixture of trialkylsilane with double the theoretical quantity of the organic acid to which the catalyst had been added. The heating was carried out until the complete cessation of evolution of the hydrogen which was always formed in

the theoretical quantity. After distilling off the excess acid, the reaction mixture was distilled over metallic copper (to eliminate free iodine) and rectified in a column. The high-boiling trialkylacyloxysilanes were vacuum distilled.

The yields of trialkylacyloxysilanes amounted to 81-87% of the theoretical when they were synthesized by the indicated method.

TABLE 1

Data on the Experiments Involving the Reaction of Trialkylsilanes with Monocarboxylic Acids

Starting Materials *		Maximum temperature of the mixture toward the end of the reaction.	Duration of the reaction (in hours).	Yield of R'COOSiR ₃ (in %)
R ₃ SiH R =	R'COOH R' =			
C ₂ H ₅	CH ₃	174°	2.5	86.4
C ₂ H ₅	C ₂ H ₅	190	1.0	85.1
C ₂ H ₅	n-C ₃ H ₇	207	3.0	82.0
C ₂ H ₅	(CH ₃) ₂ CH	200	1.0	83.7
C ₂ H ₅	n-C ₄ H ₉	230	2.5	83.2
C ₂ H ₅	(CH ₃) ₂ CHCH ₂	220	4.0	84.0
C ₂ H ₅	C ₂ H ₅ (CH ₃)CH	220	2.0	83.3
C ₂ H ₅	(CH ₃) ₃ C	208	1.5	87.8
C ₂ H ₅	n-C ₆ H ₁₁	245	2.0	85.0
C ₃ H ₇	C ₆ H ₅ CH ₂	275	1.5	81.0
C ₂ H ₅	C ₆ H ₅	265	1.5	81.6
n-C ₃ H ₇	n-C ₄ H ₉	290	1.5	85.9
n-C ₃ H ₇	(CH ₃) ₂ CHCH ₂	272	1.0	83.7
n-C ₃ H ₇	C ₂ H ₅ (CH ₃)CH	265	1.5	85.1
n-C ₃ H ₇	(CH ₃) ₃ C	255	1.5	87.1
n-C ₄ H ₉	n-C ₄ H ₉	295	1.5	86.9
n-C ₄ H ₉	(CH ₃) ₂ CHCH ₂	280	1.0	85.9
n-C ₄ H ₉	C ₂ H ₅ (CH ₃)CH	269	1.5	86.6
n-C ₄ H ₉	(CH ₃) ₃ C	255	1.5	86.9

* The molar ratio R₃SiH : R'COOH : AlI₃ = 1 : 2 : 0.04;

The data presented in Table 1 (the yields of trialkylacyloxysilanes, the duration of the reaction and the maximum temperature of the reaction mixture), show that the rate of the reaction of trialkylsilanes with monocarboxylic acids is practically independent of the structure of both components. This sharply differentiates the reaction of trialkylsilanes with organic acids from their reaction with alcohols [1]. It can also be noted that in the case of aliphatic monocarboxylic acids, the increase in the dissociation constant of the acid leads to an increase in the rate of their reaction with trialkylsilanes. Trimethylacetic acid, which has the greatest dissociation constant, reacts energetically with triethylsilane even without heating.

We did not succeed in preparing triethylformoxysilane by the reaction of triethylsilane with formic acid. Although the reaction proceeded with the evolution of hydrogen, the basic reaction product proved to be hexaethyldisiloxane.

As a result of the present investigation, we synthesized 19 trialkylacyloxysilanes R'COOSiR₃, in which R = C₂H₅, n-C₃H₇ and n-C₄H₉, while R' is a primary, secondary or tertiary alkyl radical, C₆H₅ or C₆H₅CH₂. The physical properties of these compounds, of which 16 had been previously unknown, are presented in Table 2.

Trialkylacyloxysilanes are colorless liquids with a characteristic, pleasant odor, rather difficultly hydrolyzed by water (they are more readily hydrolyzed by alcoholic solutions of alkali which we used as the basis of their quantitative determination).

The mechanism of the reaction of trialkylsilanes with carboxylic acids which is catalyzed by a mixture of iodine and aluminum (i.e., $\text{AlI}_3 + \text{I}_2$) is presented by us in the following manner.

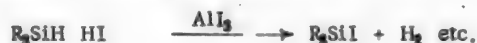
Trialkylsilane reacts with iodine with the formation of trialkyliodosilane:



The thereby-formed hydrogen iodide, in the presence of AlI_3 , quickly reacts with trialkylsilane, also with formation of trialkyliodosilane:



In the absence of AlI_3 , the latter reaction does not proceed so smoothly, which explains the smaller yields of trialkylacyloxysilanes in the reaction of trialkylsilanes with acids in the presence of iodine alone. Trialkyliodosilane then reacts with carboxylic acid with the formation of trialkylacyloxysilane and HI, which then reacts with the trialkylsilane:



The reaction of trialkyliodosilane with acid precedes its solvolytic ionization which occurs the more readily, the less the ionization constant of the acid. Due to this, the reaction proceeds as a monomolecular nucleophile substitution ($\text{S}_{\text{N}}1$ of Ingold-Hughes):



The scheme presented for the mechanism of the reaction explains the lack of dependence of the rate of the reaction of trialkylsilanes, R_3SiH , with monocarboxylic acids, RCOOH , on the structure of the R and R' radicals, since the reaction of the RCOOI^- ion proceeds from the apex of the R_3Si^+ tetrahedron which is formed after the removal of the I^- ion. In contrast to this, in the reaction of trialkylsilanes with alcohols, due to the difficulty of cleaving the hydride ion, the reaction proceeds as a bimolecular nucleophile substitution ($\text{S}_{\text{N}}2$); under these conditions the alkoxy group is forced to approach the silicon atom from the side of the alkyl groups, i.e., from the opposite side of the tetrahedral molecule R_3SiH , * which involves steric hindrance which increases with increasing size of either the alkyl radicals or of the alkoxy group.

EXPERIMENTAL

The initial trialkylsilanes, their constants and analytical data have been described in one of the preceding works [27]. The monocarboxylic acids were purified by fractional distillation in a column or in a vacuum. 78% formic acid was purified by a single freezing out, after which it was vacuum distilled over phosphoric anhydride. Before distilling the acetic acid, it was purified by a two-fold freezing out. The physical constants of the acids used are presented in Table 3.

The method of analysis for silicon and the determination of the physical constants are also described in one of our works [28].

The ester number of the trialkylacyloxysilanes was determined by saponification of samples of the substances with an 0.75 N KOH solution in ethylene glycol [29].

Method of conducting the reaction

All the syntheses of trialkylacyloxysilanes were carried out in two-necked 100 ml round-bottomed flasks

* The tetrahedral structure of the R_3SiH molecule has been confirmed by the data of the measurements of its dipole moments [26].

TABLE 2

Physical Properties of the R' — C(=O) — OSiR₃ Trialkylacyloxyulanes, Their Analytical Data and Molecular Weight Determinations

R'COOSiR ₃	b.p.	Pressure (in mm)	d ₄ ²⁰	n _D ²⁰	n _F ²⁰ - n _C ²⁰	γ ²⁰ dynes/cm	Molecular Weight		Ester number		Analysis	
							Calcu- lated	Found	Calcu- lated	Found	Calcu- lated	Found
CH ₃ COOSi(C ₂ H ₅) ₃	173.4*	760	0.8926	1.4190	0.0080	24.45	174.31	171.1; 172.3	321.32	319.0; 317.2	16.10	15.97; 15.95
CH ₃ CH ₂ COOSi(C ₂ H ₅) ₃ ..	189.1	760	0.8918	1.4220	0.0079	25.54	188.34	185.9; 184.4	297.38	293.8; 290.0	14.90	14.79; 14.62
CH ₃ (CH ₂) ₂ COOSi(C ₂ H ₅) ₃ ..	207.8	760	0.8869	1.4252	0.0082	25.00	202.37	200.3; 199.4	276.76	273.8; 276.6	13.86	13.68; 13.65
(CH ₃) ₂ CHCOOSi(C ₂ H ₅) ₃ ..	200.0	760	0.8790	1.4209	0.0076	24.32	202.37	200.0; 198.4	276.76	271.9; 271.7	13.86	13.79; 13.68
CH ₃ (CH ₂) ₃ COOSi(C ₂ H ₅) ₃ ..	225.9	760	0.8812	1.4280	0.0080	26.27	216.39	214.4; 216.8	258.82	255.9; 253.4	12.96	12.84; 12.93
(CH ₃) ₂ CHCH ₂ COOSi(C ₂ H ₅) ₃ ..	219.1	760	0.8781	1.4260	0.0078	24.93	216.39	213.4; 213.8	258.82	256.3; 251.3	12.96	12.79; 12.76
CH ₃ (C ₂ H ₅)CHCOOSi(C ₂ H ₅) ₃ ..	218.3	760	0.8786	1.4260	0.0083	25.40	216.39	214.4; 214.2	258.82	256.1; 253.0	12.96	12.67; 12.68
(CH ₃) ₂ CCOOSi(C ₂ H ₅) ₃ ..	205.4	760	0.8683	1.4200	0.0075	23.80	216.39	214.2; 213.8	258.82	256.8; 255.1	12.96	12.80; 12.76
CH ₃ (CH ₂) ₄ COOSi(C ₂ H ₅) ₃ ..	241.6	760	0.8799	1.4309	0.0078	25.96	230.42	228.5; 227.0	243.06	241.9; 239.3	12.18	11.96; 11.95
C ₆ H ₅ CH ₂ COOSi(C ₂ H ₅) ₃ ..	139.5—141.0	8	0.9872	1.4875	0.0126	28.78	250.41	249.1; 247.6	223.66	220.3; 224.4	11.20	11.03; 10.96
C ₆ H ₅ COOSi(C ₂ H ₅) ₃	133.0	8	0.9881	1.4930	0.0139	31.58	236.38	233.5; 233.3	236.93	236.0; 233.2	11.87	11.70; 11.66
CH ₃ (CH ₂) ₃ COOSi(C ₃ H ₇) ₃ ..	120.0—120.5	6	0.8726	1.4350	0.0078	25.77	258.47	255.9	216.68	214.4; 214.3	10.86	10.70; 10.69
(CH ₃) ₂ CHCH ₂ COOSi(C ₃ H ₇) ₃ ..	114.0—114.5	6	0.8704	1.4331	0.0081	25.26	258.47	253.5	216.68	214.4; 212.2	10.86	10.68; 10.66
CH ₃ (C ₂ H ₅)CHCOOSi(C ₃ H ₇) ₃ ..	112.0—112.5	5	0.8715	1.4330	0.0077	25.62	258.47	253.6	216.68	214.0; 213.0	10.86	10.65; 10.62
(CH ₃) ₂ CCOOSi(C ₃ H ₇) ₃ ..	100.0 101.0	5	0.8643	1.4291	0.0079	24.56	258.47	256.9	216.68	214.3; 216.7	10.86	10.77; 10.72
CH ₃ (CH ₂) ₃ COOSi(C ₄ H ₉) ₃ ..	143.5—144.0	5	0.8710	1.4400	0.0072	26.94	300.54	299.5	186.34	184.9; 185.6	9.33	9.20; 9.17
(CH ₃) ₂ CHCH ₂ COOSi(C ₄ H ₉) ₃ ..	40.0—140.5	5	0.8661	1.4390	0.0080	26.50	300.54	298.6	186.34	184.1; 183.0	9.33	9.12; 9.20
CH ₃ (C ₂ H ₅)CHCOOSi(C ₄ H ₉) ₃ ..	39.5—140.0	5	0.8668	1.4389	0.0078	26.65	300.54	296.6	186.34	184.7; 185.1	9.33	9.14; 9.23
(CH ₃) ₂ CCOOSi(C ₄ H ₉) ₃ ..	129.5	5	0.8623	1.4350	0.0081	25.65	300.54	296.3	186.34	184.9; 183.7	9.33	9.16; 9.23

* Previously described [16, 18, 24].

.. Previously described [9].

made of heat resistant glass, supplied with a reflux condenser and a thermometer. The upper end of the condenser was connected with a Tishchenko bottle with concentrated sulfuric acid and then with a gasometer to collect the hydrogen. 0.2 mole of the corresponding acid was placed in the reaction flask, after which a powdered mixture of 0.1 g of aluminum and 1.5 g of iodine and, finally, 0.1 mole of trialkylsilane was introduced. After this, the reaction mixture was heated until hydrogen evolution ceased and was distilled over powdered copper to eliminate the elementary iodine. The trialkylacyloxysilane thus isolated was then purified by fractional distillation.

We present the description of several synthesis as examples.

Synthesis of triethylacetoxysilane

A powdered mixture of 0.1 g of aluminum and 1.5 g of iodine was added to 12.0 g (0.2 mole) of acetic acid and then 11.6 g (0.1 mole) of triethylsilane was added. The reaction mixture was boiled until the hydrogen evolution completely ceased, which required 2.5 hours. In the course of this period, 2.6 liters of hydrogen was evolved, while the boiling point of the mixture rose to 174°. By distilling the reaction mixture over powdered copper, 6.1 g of acetic acid with a b.p. of 118.0-119.0° (755 mm) and 15.0 g of triethylacetoxysilane with a b.p. of 172.0-173.2° (755 mm) were obtained. After a second fractional distillation, the triethylacetoxysilane had a b.p. of 173.2° (754.7 mm) and had the constants presented in Table 2.

On conducting the reaction of triethylsilane with acetic acid in the presence of iodine as the catalyst, the yield of triethylacetoxysilane amounted to 69% under analogous conditions, while in the presence of sulfuric acid it amounted to 30% of the theoretical. Triethylsilane does not react with acetic acid in the presence of anhydrous aluminum chloride.

Synthesis of triethyltrimethylacetoxysilane.

A powdered mixture of 0.1 g of aluminum and 1.5 g of iodine and then 11.6 g (0.1 mole) of triethylsilane was added to 20.4 g of trimethylacetic acid. In 2-3 minutes after mixing the components, the reaction mixture spontaneously became heated to 130°, and hydrogen was evolved.

The reaction mixture was then periodically (every 10-15 minutes) heated until the hydrogen evolution completely ceased, which required 1.5 hours. After this period, 2.5 liters of hydrogen had been evolved and the temperature of the reaction mixture had risen to 208°. A repeated fractional distillation of the reaction mixture gave 10.3 g of the initial trimethylacetic acid with a b.p. of 163.0-164.2° (759 mm) and 14.0 g of triethyltrimethylacetoxysilane with a b.p. of 204.0-205.5° (759 mm), i.e., 87.8% of the theoretical.

Synthesis of Triethylbenzooxysilane

A powdered mixture of 0.1 g of aluminum and 1.5 g of iodine and then 11.6 g (0.1 mole) of triethylsilane was added to 24.4 g (0.2 mole) of fused benzoic acid. After heating the reaction mixture for 1.5 hours, its temperature had risen to 265°; at the same time, 2.3 liters of hydrogen had been evolved. By vacuum distilling the reaction mixture, 9.0 g of the initial benzoic acid with a b.p. of 118-119° (5 mm) and 23 g of the crude triethylbenzooxysilane with a b.p. of 132-133° (8 mm), containing free benzoic acid, were obtained. After purification from the admixture of benzoic acid by freezing out, the triethylbenzooxysilane was again fractionally distilled in a vacuum, after which it had a b.p. of 133.0° at 8 mm.

Freezing out in the purification of triethylphenylacetoxysilane from admixture of phenylacetic acid was used in the same way.

Synthesis of tri-n-butylisovaleroxysilane

20.4 g (0.2 mole) of isovaleric acid, 0.1 g of aluminum, 1.5 g of iodine and 20.0 g (0.1 mole) of tri-n-butylsilane were heated while being constantly stirred until evolution of hydrogen ceased, which took 1 hour. 2.4 liters of hydrogen was evolved under these conditions. After distilling off the valeric acid, 5.3 g of which came over at 175-176°, the residue was vacuum distilled. 12.9 g of tri-n-butylisovaleroxysilane with a b.p. of 140.0-140.5° (5 mm), i.e., 85.9% of the theoretical, was obtained as a result.

Synthesis of triethylacetoxysilane by the reaction of triethylsilane with mercury acetate.

11.6 g (0.1 mole) of triethylsilane was added to 31.9 g (0.1 mole) of anhydrous mercury acetate. The mixture became spontaneously heated to 86°. Upon further heating of the mixture for 40 minutes on an air bath, the boiling point of the mixture rose to 175°. Drops of metallic mercury formed on the bottom of the reaction flask. No gas evolution was observed during the reaction. The liquid reaction products were filtered off from the mercury

TABLE 3

Constants of the Initial Acids Used in the Syntheses of the Trialkylacyloxysilanes

Acid	B.p. at 760 mm	n_D^{20}	Literature data [30]		Notes	
			B.p. at 760 mm	n_D^{20}	Our data	Literature Data [30]
HCOOH	101.1	—	100.75	—	d_4^{20} 1.2206	d_4^{20} 1.22036
CH ₃ COOH	117.9	1.3740	118.1	1.37151	—	—
CH ₃ CH ₂ COOH	140.7	1.3867	141.22	1.38623	—	—
CH ₃ CH ₂ CH ₂ COOH	163.7	1.3980	164.05	1.39796	—	—
(CH ₃) ₂ CHCOOH	154.4	1.3941	154.70	1.39300	—	—
CH ₃ (CH ₂) ₃ COOH	185.6	1.4090	186.35	1.40800	—	—
(CH ₃) ₂ CHCH ₂ COOH	176.4	1.4033	176.5	1.40331	—	—
C ₂ H ₅ CH(CH ₃)COOH	176.5	1.4060	177.0	1.4051	d_4^{20} 0.9361	—
(CH ₃) ₃ CCOOH	163.7-163.9	—	163.7-163.8	—	M.p. 35.5- 35.7°	M.p. 35.3- 35.5°
CH ₃ (CH ₂) ₄ COOH	204.0	1.4170	205.15	1.4170	—	—
C ₆ H ₅ CH ₂ COOH	126.5-127.1 (5 mm)	—	144.5 (12 mm)	—	M.p. 76.6°	M.p. 76.5°
C ₆ H ₅ COOH	118.7-119.3 (5 mm)	—	—	—	M.p. 122.0°	M.p. 122.305°

and its salts, which were then washed with ether. The filtrate was fractionally distilled after preliminary elimination of the ether. 5.4 g of acetic acid with a b.p. of 118-120° (758 mm) and 12.7 g of triethylacetoxysilane with a b.p. of 172-174° (758 mm) were thereby obtained. The yield of triethylacetoxysilane amounted to 72.5% of the theoretical. After a repeated fractional distillation, it had a b.p. of 173.3° (752.1 mm); d_4^{20} 0.8925; n_D^{20} 1.4190.

Found%: Si 15.82, 15.86; ester number 318.5, 317.2; CH₃COOSi(C₂H₅)₃. Calculated %: Si 16.10; ester number 321.3.

Literature data for triethylacetoxysilane: Ladenburg [18] —b.p. 168°; d_4^{20} 0.9039; Sommer and others [24] —b.p. 167° (726 mm).

The physical constants of the triethylacetoxysilane obtained are in excellent agreement with the constants of this compound which we obtained by the reaction of triethylsilane with acetic acid (Table 2). This indicates that the triethylacetoxysilane, obtained by the methods described previously [18,24], apparently contained an admixture, since it had a boiling point 5-6° lower. *

SUMMARY

A new method for the synthesis of trialkylacyloxysilanes by the reaction of trialkylsilanes with organic acids in the presence of catalyst was worked out. 19 compounds of this type, 16 of which had not been known previously, were synthesized by this method in a yield of 81-87%, and their physical properties were determined. It was found that the course of the reaction of trialkylsilanes with carboxylic acids is only slightly dependent on the structure of the trialkylsilane and acid. A scheme for the mechanism of the reaction was proposed. It was shown that trialkylacyloxysilanes can also be prepared by the reaction of trialkylsilanes with mercury salts of carboxylic acids.

* Larsson [16], in a work which recently became accessible to us, gives a b.p. of 175-177° for triethylacetoxysilane.

LITERATURE CITED

- [1] M. G. Voronkov, *Chemistry of Silicoorganic Compounds in the Works of Russian and Soviet Scientists*, p. 53, Leningrad State University Press, 1952.
- [2] A. F. Reilly, H. W. Post, *J. Org. Ch.*, **16**, 387 (1951).
- [3] H. Kautsky, A. Hirsch, *Z. anorg. Chem.*, **170**, 1 (1928).
- [4] S. Nitzsche, *Angew. Chem.*, **63**, 490 (1951).
- [5] C. Friedel, A. Ladenburg, *Ann.*, **145**, 174 (1868).
- [6] K. D. Petrov, M. I. Itkina, *J. Gen. Chem.*, **17**, 220 (1947).
- [7] K. D. Petrov, *J. Gen. Chem.*, **17**, 1099 (1947).
- [8] Yu. K. Yuryev G. B. Elyakov, *Proc. Acad. Sci. USSR* **86**, 337 (1952).
- [9] D. N. Andreev, L. L. Shchukovskaya, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, No. 1, 135 (1953).*
- [10] C. A. Mackenzie, M. Schoffman, U. S. Patent 2537073; *C. A.*, **45**, 3410 (1951); C. A. Mackenzie, U.S. Patent 2566347 (1951); *C. A.*, **46**, 4560 (1952).
- [11] C. Pape, *Ber.*, **14**, 1872 (1881); *Ann.*, **222**, 354 (1884).
- [12] A. J. Barry, U. S. Patent 2405988 (1946); *C. A.*, **41**, 477 (1947).
- [13] H. A. Schuyten, J. W. Weaver, J. B. Reid, *J. Am. Chem. Soc.*, **69**, 2110 (1947).
- [14] C. M. Langkammer, U. S. Patent 2253128 (1941); *C. A.*, **35**, 8151 (1941).
- [15] F. C. Lanning, *J. Am. Chem. Soc.*, **75**, 1596 (1953).
- [16] E. Larsson, *Trans. Chalm. Univ.*, **25**, No. 115, 9 (1951).
- [17] Yu. N. Volnov, *J. Gen. Chem.*, **9**, 2269 (1939).
- [18] A. Ladenburg, *Ber.*, **5**, 319 (1872); *Ann.*, **164**, 300 (1872).
- [19] R. O. Sauer, W. Patnode, *J. Am. Chem. Soc.*, **67**, 1548 (1945).
- [20] C. Friedel, J. M. Crafts, *Am. Chem. Phys.*, (4), **9**, 5 (1866); *Am. J. Sci.*, [2] **43**, 331 (1867).
- [21] H. W. Post, C. H. Hofrichter, *J. Org. Chem.*, **5**, 443, (1940).
- [22] F. C. Boyd, H. W. Post, *J. Org. Chem.*, **17**, 1386 (1952).
- [23] F. S. Kipping, L. L. Lloyd, *J. Chem. Soc.*, **79**, 449 (1901); *Pr. Chem. Soc.*, **15**, 174 (1900).
- [24] L. H. Sommer, E. W. Pietrusza, F. C. Whitmore, *J. Am. Chem. Soc.*, **68**, 2282 (1946).
- [25] L. Malatesta, *Gazz.*, **78**, 753 (1948); Italian Patent 436808 (1948);
- [26] H. O. Spauschus, A. P. Mills, J. M. Scott, C. A. Mackenzie, *J. Am. Chem. Soc.*, **72**, 1377, (1950); Cf. L. Malatesta, R. Pizzoti, *Gazz.*, **72**, 491 (1942).
- [27] B. N. Dolgov, N. P. Kharitonov, M. G. Voronkov, *J. Gen. Chem.*, **24**, 678 (1954).
- [28] M. G. Voronkov, B. N. Dolgov, N. P. Zapevalova, *Sci. Rep. Leningrad State University, Chem. Series*, No. 12, 161, (1953).
- [29] L. N. Petrova, O. B. Shvarts, *Analysis of Synthetic Perfumes*, Food Industry Press, Moscow-Leningrad (1941).
- [30] J. Timmermans, *Physico-chemical constants of pure organic compounds*, Amsterdam (1950).

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SYNTHESIS AND PROPERTIES OF HEXAPHENYLDISILAZANE AND HEXA-p-TOLYLDISILAZANE

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The conditions for preparing the sole hexaaryldisilazane which is known in the literature - hexaphenyldisilazane—were indicated in the work of Reinolds and his coworkers [1]; they synthesized it by the reaction of triphenylsilane with liquid ammonia in the presence of metallic sodium. According to the data of the authors [1], this compound consists of a crystalline substance with a m.p. of 175°.

In the present work, we describe a method for preparing hexaaryldisilazanes which consists in passing gaseous ammonia into a solution of triarylfluorosilane in toluene which is heated to 100-110° in the presence of metallic lithium. Thus, for example, we obtained as a result of the reaction of triphenylfluorosilane with ammonia in the presence of lithium, crystalline hexaphenyldisilazane which was insoluble in ethyl ether, petroleum ether and ethyl alcohol, and had a m.p. of 235-236°, and not 175° as the authors [1] reported. It is pertinent to mention that its hexaphenyldisiloxane has a m.p. of 220°. [2].

The reaction of triphenylfluorosilane under the indicated conditions proceeds in the initial stages with the formation of unstable intermediate N-lithium-containing compounds which then, reacting with the initial substance, in the end yield the rather stable hexaphenyldisilazane.

The course of the reaction is represented by the following equations



Starting with tri-p-tolylfluorosilane [3] under the same conditions, we also synthesized hexa-p-tolyldisilazane—a crystalline substance with a m.p. of 225-226° (after recrystallization from toluene). Its analog—hexa-p-tolyldisiloxane—melts at 223° [4].

Attempts to prepare hexa- α -naphthyldisilazane, starting from tri- α -naphthylfluorosilane, gaseous ammonia and metallic lithium under analogous conditions, were not successful. Tri- α -naphthylaminosilane [5], which melted at 204-206°, was isolated in place of the expected product.

It should be noted that, depending on the spatial structure of the radicals directly bound to the silicon atom, the hydrogen atoms in the amino group can be replaced either by two or three silyl groups or by only one, forming the corresponding nitrogen-containing silicoorganic compounds. Thus, for example, even in the cold, chlorosilane readily reacts with ammonia, completely replacing the hydrogen atoms with silyl groups to give tri-silazane [6] according to the equation



while the reaction of trimethylchlorosilane with ammonia leads only to the formation of hexamethyldisilazane [7]. The participation of an alkali metal is still indispensable for the preparation of hexaphenyldisilazane and hexa-p-tolyldisilazane.

EXPERIMENTAL

Hexaphenyldisilazane $(\text{C}_6\text{H}_5)_3\text{SiNHSi}(\text{C}_6\text{H}_5)_3$

In a side-arm flask, equipped with a reflux condenser, 0.025 mole (6.96 g) of triphenylfluorosilane with a m.p. of 63-64°, dissolved in 50 ml of toluene and 0.1 mole of metallic lithium, cut in the form of fine flakes, were introduced. Then, while the toluene was being heated to weak effervescence, gaseous ammonia, dried over CaO and KOH, was passed into the solution for 6 hours. After some time had elapsed, the gradual formation of a flocculent

precipitate of lithium fluoride was observed in the solution; at the same time, the surface of the metallic lithium remained shiny at the end of the experiment. After cessation of the ammonia delivery, the solution was boiled for 1 hour more to complete the reaction, and then the precipitate was filtered off while hot. 4.2 g (in a yield of 32%, calculating on the basis of the initial triphenylfluorosilane) of hexaphenyldisilazane which melted at 235-236°, was isolated from the filtrate after two crystallizations from toluene. The product was practically insoluble in ethyl ether and in petroleum ether and alcohol. A mixed sample with hexaphenyldisilazane with the tetraphenylsilane [3] previously prepared by us which melted at approximately the same temperature, displayed a strong melting point depression; the mixture melted over a broad temperature range at 205-210°.

Found %: Si 10.1, 10.3; N (by Dumas' method) 2.22, 2.30; M 522, 528. $C_{36}H_{31}Si_2N$. Calculated %: Si 10.6; N 2.26; M 534.

Hexa-*p*-tolylidisilazane ($n-C_6H_4CH_2SiNH_2Si(C_6H_4CH_2)_n$) was prepared analogously from 0.025 mole of tri-*p*-tolylfluorosilane with a m.p. of 103-104° and 0.1 mole of lithium. The crystals which separated from the filtrate were again recrystallized from toluene. 3.6 g (23%) of hexa-*p*-tolylidisilazane, which melted at 223-224°, was collected.

Found %: Si 8.6, 8.7; N (by Dumas' method) 2.60, 2.42; M 613, 606. $C_{48}H_{48}Si_2N$. Calculated %: Si 9.0; N 2.62; M 617.9.

SUMMARY

A convenient method for preparing hexaphenyl- and hexatolylidisilazanes was found and a scheme for their formation was proposed. Hexa-*p*-tolylidisilazane was synthesized for the first time. The melting point of hexaphenyldisilazane was determined accurately.

Hexa-*a*-naphthyldisilazane is not formed under the indicated conditions on account of spatial complications.

LITERATURE CITED

- [1] H. H. Reynolds, L. A. Bigelow and C. A. Kraus, J. Am. Chem. Soc., 51, 3067 (1929).
- [2] W. S. Schumb and C. M. Saffer, J. Am. Chem. Soc., 61, 863 (1939).
- [3] V. S. Chugunov, Bull. Acad. Sci. USSR, Div. Chem. Sci., 1953, 860. *
- [4] A. R. Steele and F. S. Kipping, J. Am. Chem. Soc., 1939, 357.
- [5] V. S. Chugunov, J. Gen. Chem., 23, 777 (1953). **
- [6] A. Stock and K. Somieski, Ber., 54, 74 (1921).
- [7] R. O. Sauer and R. N. Hasek, J. Am. Chem. Soc., 68, 241 (1946).

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* See Consultants Bureau Translation, p. 761.

** See Consultants Bureau Translation, p. 811.

DIPOLE MOMENTS AND STRUCTURE OF CERTAIN SULFANILAMIDE COMPOUNDS

Z. V. Pushkareva and Z. Yu. Kokoshko

The problems of the detailed structure of sulfanilamide compounds are of indisputable interest due to the great practical significance of this group of medicinal substances [1,2].

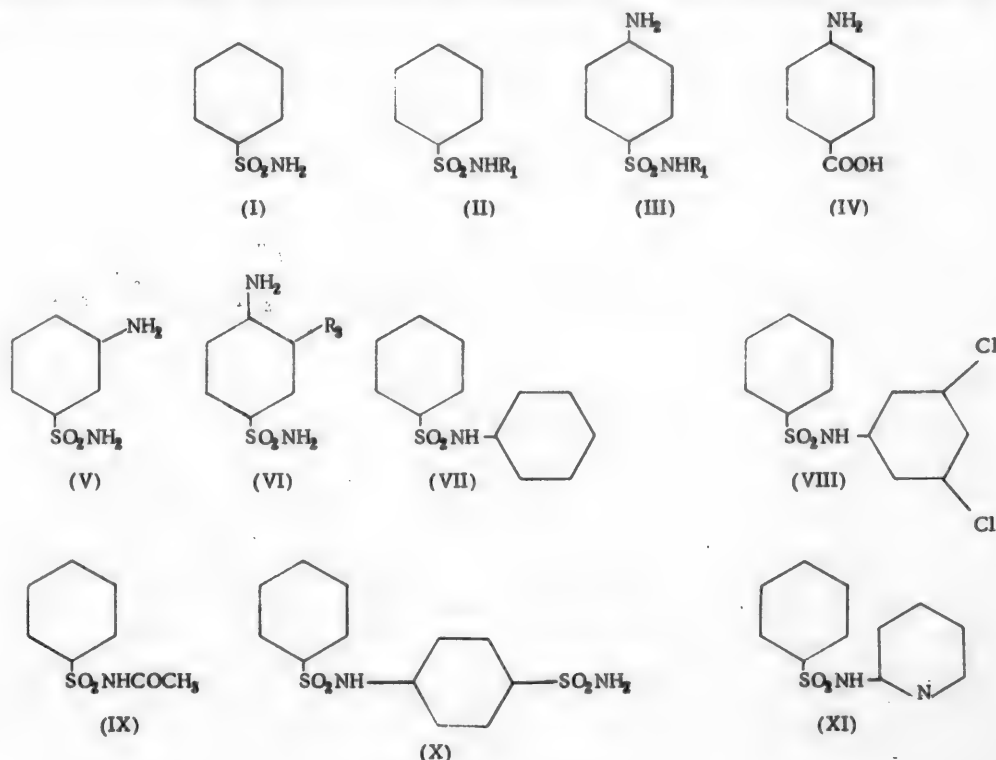
The structure of the molecules of the various sulfanilamide compounds is based on benzenesulfonamide(I).

As is well known, benzenesulfonamide derivatives acquire antibacterial, chiefly anticoccal, activity only when a primary amino group is introduced in the para position in relation to the sulfonamide group and a sulfanilamide of the general formula (III)* is formed.

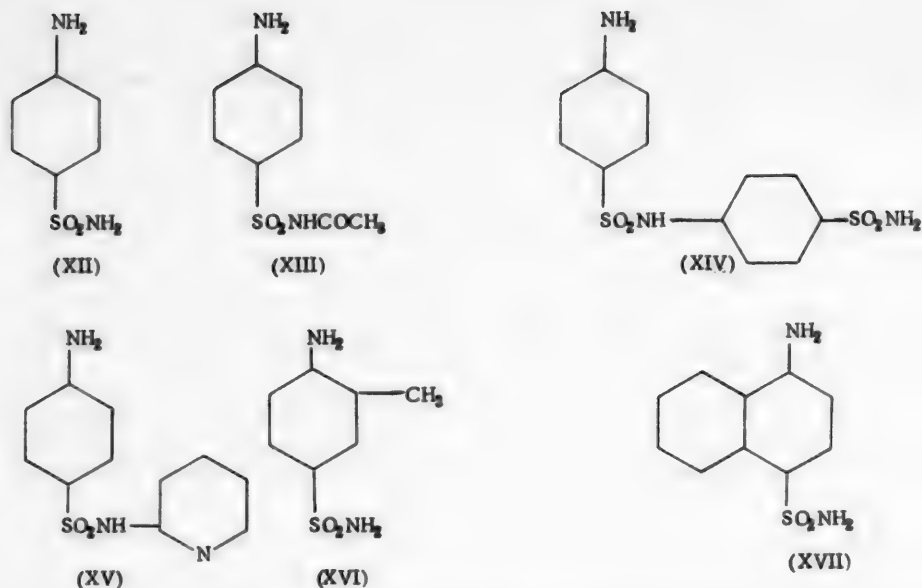
The introduction of an amino group into the meta position does not give active substances (metanilamide V). It is also known, that change in the character of R_1 in the formula (III) leads to significant changes in the activity, and sometimes to its complete suppression. Replacement of the hydrogen atoms of the benzene ring also influences the antibacterial activity (for example, the substance with formula VI).

In the present work we have attempted to elucidate the mutual dependence between such changes in structure and the values of the dipole moments of the molecules.

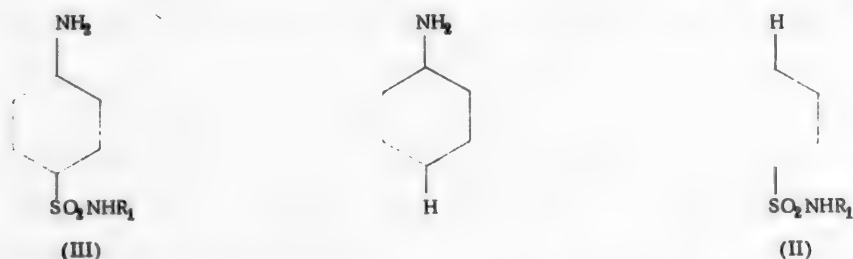
With this object, we measured the dipole moments of 12 substances, the majority of which we synthesized by methods described in the literature. The first group of compounds consists of substances of type (II), with various R_1 groups (the so-called deaminated sulfanilamides), viz.: (I); (VII), (VIII), (IX), (X), and (XI). The second group of substances consists of sulfanilamides of formula (III) but with the same R_1 substituents, i.e., of compounds (XII) [derived from (I)], (XIII) [derived from (IX)], (XIV) [derived from (X)] and (XV) [derived from (XI)].



* We have in mind the sulfanilamides proper, i.e., strictly substances with a single group with a definite action mechanism, in particular, which are capable of biological competition with p-aminobenzoic acid (IV).



We then compared the dipole moments of the sulfanilamides with the moments of molecules which contain hydrogen atoms in place of the substituents; in other words, compared the following three molecules:



Such a comparison, as is well known, can be carried out via the calculation of the vector sums of the moments for sulfanilamide (III), starting from the experimental data on the dipole moments of deaminated sulfanilamides (II) and aniline ($\mu = 1.78$ D in dioxan), and by determining the difference between the experimental and calculated values of the dipole moments.

The data obtained are presented in Tables 1, 2 and 3 for convenience.

As is evident from the data of Table 1, the dipole moments of sulfanilamides, as a rule, are greater than the simple vector sum of the moments of the substituent groups.

Inasmuch as the dipole moments of the $-NH_2$ and $-SO_2NH_2$ groups, on the basis of which the vector sums were calculated, were measured experimentally under identical conditions, while the dipole moment of unsubstituted benzene is equal to zero, the difference $\mu_{\text{exp.}} - \mu_{\text{calc.}}$ may be due only to the redistribution of the electron density in molecule (III) due to the mutual influence of the amino and sulfonamide groups. In other words, this effect of mutual influence is expressed, as it were, in an increased polarity of the "para bond" (increased, since $\mu_{\text{exp.}} - \mu_{\text{calc.}}$ is positive).

The polarity of the para bond is quantitatively characterized by the value of $\mu_{\text{exp.}} - \mu_{\text{calc.}}$ and depends on the structure of R_1 . The greatest effect of increasing the polarity of the para bond, caused by mutual influence of the para substituents, occurs when R_1 is a highly polar group with a plane structure.

The indicated effect of mutual influence of the amino and sulfonamide groups through the benzene ring is, as is evident, specific for para substitution and does not occur with meta substitution (No. 5 in Table 1, $\mu_{\text{exp.}} - \mu_{\text{calc.}} = 0$).

Substitution in the benzene ring [compounds (XVI) and (XVII)] leads to the reverse effect—to a lowering of the polarity of the para bond, which follows from the data of Table 2.

TABLE 1

Expt. No.	Sulfanilamide		Deaminated sulfanilamide		Vector sum of the moments for the sulfanilamide ($\mu_{\text{calc.}} \cdot 10^{18}$).	$\mu_{\text{exp.}} - \mu_{\text{calc.}}$
	Structure	Experimental dipole moment ($\mu_{\text{exp.}} \cdot 10^{18}$)	Structure	Experimental dipole moment ($\mu_{\text{exp.}} \cdot 10^{18}$)		
1		6.60		5.09	5.85	0.75
2		6.99		5.55	6.13	0.86
3		6.88		4.96	5.40	1.39
4		7.2		4.95	5.7	1.5
5		5.63		5.09	5.64	0.0

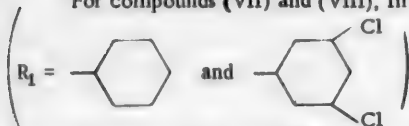
TABLE 2

Expt. No.	Substance	$\mu_{\text{exp.}} - \mu_{\text{calc.}}$
1	Sulfanilamide (XII)	0.75
2	3-Methylsulfanilamide (XVI)	0.16
3	Naphthionamide (XVII)	0.62

TABLE 3

Formula No.	$\mu_{\text{calc.}} \cdot 10^{18}$			$\mu_{\text{exp.}} \cdot 10^{18}$
	Configuration "A"	Configuration "B"	Free rotation	
(VII)	5.05	5.51	5.79	5.07
(VIII)	4.87	6.9	5.80	4.75

For compounds (VII) and (VIII), in which R_1 is comparatively simple as regards the structure of the substituent



, the method of vector sums was used to calculate the dipole moments

for configurations "A" and "B" and for the free rotation of NHR in relation to the S-N bond (Fig. 1). The data presented in Table 3 were obtained as a result.

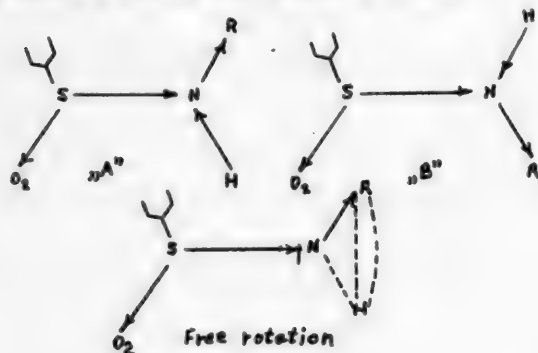


Fig. 1

It follows from these data that configuration "A", illustrated by a model of compound (VIII) (see fig. 2, p. 931) is the most probable configuration.

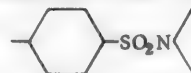
This configuration is distinguished by the fact that the hydrogen of the -NH- groups is found at the shortest of all the possible distances from the oxygen atoms of the -SO₂ groups.

EXPERIMENTAL

The dielectric constants of the substances investigated (ϵ) were determined by a heterodyne method. Benzene (ϵ^{25}_D 2.2714) was taken as a control liquid. Dioxan, carefully purified, with a solidification temperature of 11.77-11.80°, was used as the solvent.

All the determinations were carried out at $25^\circ \pm 0.02^\circ$. The density of the solutions (d) was determined; with the use of a torsion balance, at the same time as the dielectric constant. Complete polarization (R_D) was calculated by the formula of Debye in Hoderstrand's form [3] from the experimental data for ϵ and d . The electronic polarization (P_e) was calculated from the experimental values of the refraction of benzenesulfonamide, found by

Guryanova [4], since the molecules of all the substance investigated contain the



group (benzenesulfonamide radical). The refractions of the other groups in the atoms were taken from the literature data [5]. The atomic refraction was ignored. In the end, the dipole moments were measured to within ± 0.015 - 0.020 D.

The results of the measurements are placed in Table 4.

Substances

The substances of the general formula (III) were prepared by the condensation of acetaminobenzenesulfonyl chloride with the corresponding amines in a pyridine solvent. The acetyl derivatives obtained were then saponified to the free amine.

The deaminated products of the general formula (II) were prepared by the condensation of benzenesulfonyl chloride with the amines.

The substances were purified by crystallization from water or ethyl alcohol.

N-Phenylbenzenesulfonamide (VII). It was prepared by the condensation of pure benzenesulfonyl chloride with aniline purified, by crystallization from aqueous alcohol, to a constant melting point which was in accord with the literature data (109-110°).

N-3,5-Dichlorophenylbenzenesulfonamide (VIII). It was prepared by the condensation of benzenesulfonyl chloride with 3,5-dichloroaniline. The latter was synthesized from p-nitroaniline by the method described [6]. 9.5 g of dichloroaniline was dissolved in 54 ml of dry pyridine bases and a solution of 12 g of benzenesulfonyl chloride in 40 ml of acetone was added to the solution while it was being stirred. The mixture was stirred for 1 hour and diluted with cold water. The precipitate was filtered off, dissolved in 1 N NaOH, and the solution was acidified with hydrochloric acid. The precipitate which settled out was filtered off and recrystallized from aqueous alcohol. The yield was 26%.

On the basis of its melting point, the product was identified as the described N-3,5-dichlorophenylbenzenesulfonamide (constant m.p. at 134-135°).

TABLE 4

Results of measurement of dipole moments.

Expt. No.	Compound	P_{∞}	P_e	$\mu \cdot 10^{18}$
1	Benzenesulfonamide (I)	571.39	40.13	5.09
2	N-Phenylbenzenesulfonamide (VII)	595.34	64.22	5.07
3	N-3,5-Dichlorophenylbenzenesulfonamide (VIII)	539.08	73.85	4.75
4	N-p-Sulfonamidophenylbenzenesulfonamide (deaminated disulfane) (X)	714.82	78.06	5.55
5	N-Acetylbenzenesulfonamide (deaminated sulfacil) (IX)	558.14	49.37	4.96
6	N-(α -Pyridyl)-benzenesulfonamide (deaminated sulfidine) (XI)	573.51	65.76	4.95
7	Sulfanilamide (XII)	—	—	6.60
8	3-Methylsulfanilamide (XVI)	808.14	48.27	6.06
9	Naphthionamide (XVII)	943.94	61.09	6.53
10	N'-Acetylsulfanilamide (sulfacil) (XIII)	1030.45	58.80	6.88
11	N'-(α -Pyridyl)-sulfanilamide (sulfidine) (XV)	1189.56	69.08	7.2
12	N'-p-Sulfonamidophenylsulfanilamide (disulfane)	1090.78	82.58	6.99

N-p-sulfonamidophenylbenzenesulfonamide (X) (deaminated disulfane). It was prepared by the condensation of streptocidin with benzenesulfonyl chloride in an aqueous medium. It was purified by recrystallization from water and alcohol and melted at 148°.

5.320 mg sub.; 0.4214 ml N_2 (17°, 734 mm). 3.985 mg sub.; 0.3332 ml N_2 (24°, 737 mm). Found %: N 9.0, 9.32. Calculated %: N 9.30.

N-Acetylbenzenesulfonamide (IX) (deaminated sulfacil); It was prepared by the acetylation of benzenesulfonamide with acetic anhydride. It was purified by repeated crystallization from water and alcohol (m.p. 122°).

N'-(α -Pyridyl)-benzenesulfonamide (XI) (deaminated sulfidine). It was prepared by condensing α -aminopyridine with benzenesulfonyl chloride in pyridine bases. It was purified by recrystallization from alcohol; the m.p. of 171-172° was in accord with the literature data.

3-Methylsulfanilamide (XVI). Toluidine was acetylated with acetic anhydride in the usual manner, and the acetyl-o-toluidine was chlorosulfonated with a 5-fold quantity of chlorosulfonic acid at 60-70° for 2 hours. The sulfonyl chloride of acetyl-o-toluidine was amidated with aqueous ammonia. The melting point of the unpurified amide was 202-204° and the yield 50%. The 3-methylacetylsulfanilamide obtained was added during stirring to a solution of 15 ml concentrated sulfuric acid in 50 ml of water which was heated to 80°. The mixture was heated on a boiling water bath for an hour and a half. The cooled mixture was filtered and 3-methylsulfanilamide was precipitated from the filtrate with ammonia. The latter was filtered off and recrystallized from water. The yield was 75%. The product was finally purified by 3-fold crystallization from water; the m.p. was 145-146°.

4.637 mg sub; 0.627 ml N_2 (19°, 734 mm). Found %: N 15.29. Calculated %: N 15.04

The Naphthionamide (XVII) was left by us for determination by B. G. Boldyrev. It was purified by recrystallization from alcohol to constant melting point (212°). In view of the insignificant decomposition on fusion, the purity of the product was additionally verified by analysis.

4.95 mg sub.; 0.5684 ml N_2 (23°, 735 mm). 5.28 mg sub; 0.5880 ml N_2 (21°, 749 mm). Found %: N 12.61, 12.64. Calculated %: N 12.61.

N'-Acetylsulfanilamide (IX) (sulfacil) The commercial product was subjected to 2-fold purification via the sodium salt; the m.p. was 182°.

N'-p-Sulfonamidophenylsulfanilamide (XIV) (disulfane). Commercial disulfane was purified via the sodium salt and repeatedly crystallized from water; in view of the diffuseness of the melting point, the purity of the substance was verified by analysis for nitrogen.

3.943 mg sub.: 0.440 ml N_2 (16°, 729 mm). 6.271 mg sub.: 0.726 ml N_2 (20°, 730 mm). Found %: N 12.82, 12.96. Calculated %: N 12.82.

Sulfidine (XV). The commercial product was crystallized three times from very large quantities of alcohol. The constant m.p. was 192°.

SUMMARY

1. The dipole moments of 12 substances of the sulfanilamide type were measured.
2. The presence of a specific mutual influence effect between the $-NH_2$ and $-SO_2NHR$ groups in the para position to each other, was demonstrated by comparison of the experimental dipole moments with the moments calculated by the vector addition method.

LITERATURE CITED

- [1] N. A. Preobrazhensky and A. G. Natradze, *Prog. Chem.*, 15, 4, 427 (1946).
- [2] E. N. Northey, *Chem. Rev.*, 27, 85 (1940).
- [3] Hodestrand, *Z. phys. Chem.*, 2, 428 (1929).
- [4] E. N. Guryanova, *J. Phys. Chem.*, 21, 411 (1947).
- [5] Ch. F. Smaïs, *Dielectric Constants and the Structure of Molecules* (1937).
- [6] Witt, *Ber.*, 36, 4391 (1903); 42, 2953 (1909).

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DIPOLE MOMENTS AND THE STRUCTURE OF CERTAIN ACRIDINE DERIVATIVES

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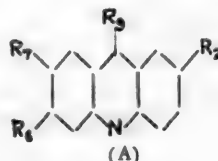
Among the derivatives of acridine (I), there is a whole series of valuable medicinal substances, including antimalarials of the atebirin(XV) type.

Inasmuch as the polarity of the molecules of medicinal substances is, in many cases, an important factor in their specific structure, in addition to the dipole moment measurements previously published [1,2], in the present work we measured the dipole moments of 12 substances which are either antimalarial compounds, or simple molecules which, however, include in themselves the structural elements of compounds of the atebirin type.

On the whole, the substances were selected in such a way that it would be possible to clarify the effect of the influence of the separate substituents on the polarity of the acridine molecule of the general formula (A). At the same time, we studied the influence on the polarity of those substituents which either cause the antimalarial activity of the acridine molecule (for example $R_4 = OCH_3$, $R_6 = Cl$, $R_9 = NHR$ and so forth), or, on the other hand, yield inactive substances (for example, $R_7 = NO_2$ and others).

The measurement of the dipole moments of substances (XIX) and (XX) was necessary for calculating the vector sums.

To clarify the influence of the separate substituents on the polarity of the acridine molecules, it was necessary to have an acridine compound with a zero dipole moment. Precisely such an acridine derivative is 9-chloroacridine, the dipole moment of which was measured by us previously [1] and proved to be equal to zero. By introducing various substituents into the molecule of 9-chloroacridine, we obtained compounds, the magnitudes of the dipole moments of which characterized the influence of the corresponding substituents on the polarity of the molecule.



The dipole moments were measured by a heterodyne method in benzene solutions at 25° and the density of the solutions was determined with the aid of a torsion balance at the same time.

The complete polarization at infinite dilution (P_{∞}) and the dipole moments (μ_{exp}) were calculated by the generally accepted method of Hodestrand [3]. The values of the electronic polarization (P_e) were calculated from the experimental data on the refractions. The errors in the measurements of the dipole moments amounted to ± 0.02 D.

The vector sums of the moments of the bonds ($\mu_{calc.}$) were calculated for comparison with the experimental values.

For the most part, we synthesized the substances for the investigations by the described methods, sometimes adapted, and carefully purified them by recrystallization from the corresponding pure solvents (the melting points of the substances investigated by us are presented in Table 1). Substances (V), (XV), (XVI), (XVII), (XVIII) were kindly submitted to us for the measurements by A. M. Grigorovskiy.

The results of the measurements and the calculations of the dipole moments are presented in Table 1.

DISCUSSION OF RESULTS

The aggregate data on the dipole moments are grouped in Table 2 according to type of substitution in the molecule of the general formula (A) for simplicity.

In discussing the data set forth in Table 2, we start from the fact that the difference between the experimental values of the dipole moments and the vector sums of the moments of the bonds appears to be a result of the mutual influence of the atoms and groups present in the molecule, and characterizes the given mutual influence effect. The following conclusions and assumptions can be drawn and made from the data of the table.

1. A methoxy group in the 2-, and a chlorine in the 6- position approximately identically increase the polarity of the 9-chloroacridine molecule. Their simultaneous presence in positions 2 and 6 does not cause a significant additional mutual influence effect ($\mu_{exp} - \mu_{calc.} = 0.46, 0.47$ and 0.62 D respectively).

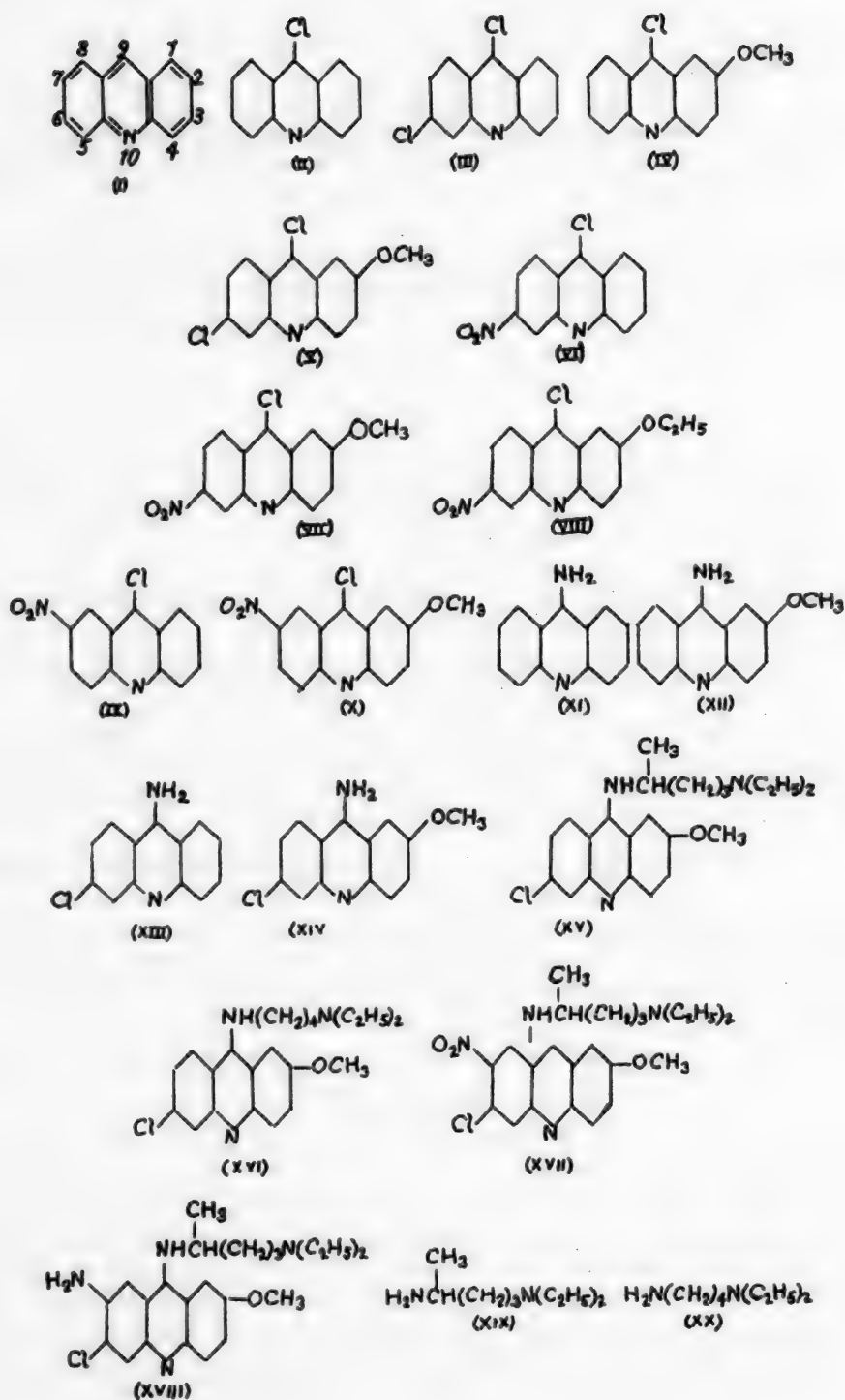


TABLE 1

Formula No. in the text	Substance	M.p.	P_{∞}	P_e	$\mu_{\text{exp.}} \cdot 10^{18}$
(VI)	6-Nitro-9-chloroacridine	214°	542.54	79.54	4.98
(VII)	2-Methoxy-6-nitro-9-chloroacridine	208	893.81	84.87	6.26
(VIII)	2-Ethoxy-6-nitro-9-chloroacridine	189-191	836.85	90.25	6.01
(IX)	7-Nitro-9-chloroacridine	203-204	503.66	79.54	4.53
(X)	2-Methoxy-7-nitro-9-chloroacridine	224	621.93	87.87	5.10
(XV)	Atebrin (base)	88	806.75	131.47	5.72
(XVI)	Atebrin No. 8 (base)	78-81	847.94	128.53	5.90
(XVII)	7-Nitroatebrin (base)	—	1110.93	133.97	6.88
(XVIII)	7-Aminoatebrin (base)	—	685.33	137.91	5.16
(XX)	1-Diethylamino-4-aminopentane	—	89.50	51.08	1.36
(XXI)	1-Diethylamino-4-aminobutane	—	75.24	46.45	1.20

2. A nitrogroup in position 7, and, in particular, in position 6, markedly increases the dipole moment of the 9-chloroacridine molecule ($\mu_{\text{exp.}} = 4.53$ and 4.98 D; $\mu_{\text{exp.}} - \mu_{\text{calc.}} = 0.58$ and 1.03 D respectively).

A considerable mutual influence effect is manifested upon the simultaneous introduction of a methoxy or ethoxy group into position 2, and a nitro group into position 6 ($\mu_{\text{exp.}} - \mu_{\text{calc.}} = 1.74$ and 1.46 D) and a somewhat smaller effect is manifested in 2-methoxy-7-nitro-9-chloroacridine ($\mu_{\text{exp.}} - \mu_{\text{calc.}} = 0.96$ D).

3. 9-Amino substitution in the acridine molecule leads to a dipole moment of 4.13 D and $\mu_{\text{exp.}} - \mu_{\text{calc.}} = 0.85$ D. The additional introduction of a methoxy group into position 2 of 9-aminoacridine and of chlorine into position 6 does not cause any particular effect, and the difference between the experimental values of the dipole moments and the vector sums is equal to 0.65 and 0.59 D respectively. With the simultaneous introduction of all three substituents (the so-called "atebrinic" type of substitution), the dipole moment is increased to 6.73 D ($\mu_{\text{exp.}} - \mu_{\text{calc.}} = 1.78$).

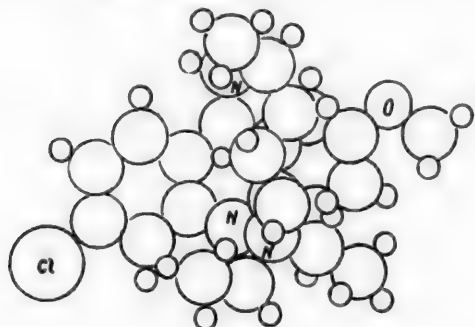


Fig. 3

4. The introduction of alkylaminoalkyl radicals into the 9-amino group, in all the cases investigated by us (XV, XVI, XVII and XVIII), leads to a lowering of the dipole moment (the solubility of the substances in benzene and their capacity to form hydrates is correspondingly sharply increased) in comparison with 2-methoxy-6-chloro-9-aminoacridine (XIV). For atebrin (XV), we calculated the vector sums of the bond moments of various molecular configurations, depending on the location of the alkyl-aminoalkyl "chainlet", which configurations are depicted in Figs. 1,2,4 (see plate, page 931.).

Comparison of the vector sums with the experimental values for the dipole moments permits us to assume that there is no free internal rotation of the -NHR dipole in such compounds as these, while there occurs some sort of definite steric interaction of the diethylamino groups of the diethyl-aminoalkyl radical with other polar groups of the atebrin molecule, which is hard to determine with only the aid of the dipole moments.

SUMMARY

1. The dipole moments of 12 substances of the acridine series were determined.
2. A comparison of the dipole moment values obtained with the corresponding vector sums of the bond moments, revealed mutual influence effect of the substituents in definite positions of the acridine ring.

TABLE 2

Formula No. in the text	R ₂	R ₆	R ₇	R ₉	$\mu_{\text{exp}} \cdot 10^{18}$	Vector sum of the bond moments	$\mu_{\text{exp}}^{\text{calc}}$
(II)*	H	H	H	Cl	0	0	0
(III)*	H	Cl	H	Cl	2.01	1.55	0.46
(IV)*	OCH ₃	H	H	Cl	1.70	1.23	0.47
(V)*	OCH ₃	Cl	H	Cl	2.91	2.29	0.62
(VI)	H	NO ₂	H	Cl	4.98	3.95	1.03
(VII)	OCH ₃	NO ₂	H	Cl	6.26	4.52	1.74
(VIII)	OC ₂ H ₅	NO ₂	H	Cl	6.01	4.55	1.46
(IX)	H	H	NO ₂	Cl	4.53	3.95	0.58
(X)	OCH ₃	H	NO ₂	Cl	5.10	4.14	0.96
(XI)*	H	H	H	NH ₂	4.13	3.28	0.85
(XII)*	OCH ₃	H	H	NH ₂	4.65	4.00	0.65
(XIII)*	H	Cl	H	NH ₂	4.84	4.25	0.59
(XIV)*	OCH ₃	Cl	H	NH ₂	6.73	4.95	1.78
(XV)	OCH ₃	Cl	H	$\begin{array}{c} \text{CH}_3 \\ \\ \text{NHCH}(\text{CH}_2)_3\text{N}(\text{C}_2\text{H}_5)_2 \end{array}$	5.72	4.55	1.17
(XVI)	OCH ₃	Cl	H	$\text{NH}(\text{CH}_2)_4\text{N}(\text{C}_2\text{H}_5)_2$	5.90	4.43	1.47
(XVII)	OCH ₃	Cl	NO ₂	$\begin{array}{c} \text{CH}_3 \\ \\ \text{NHCH}(\text{CH}_2)_3\text{N}(\text{C}_2\text{H}_5)_2 \end{array}$	6.88	5.68	1.20
(XVIII)	OCH ₃	Cl	NH ₂	$\begin{array}{c} \text{CH}_3 \\ \\ \text{NHCH}(\text{CH}_2)_3\text{N}(\text{C}_2\text{H}_5)_2 \end{array}$	5.16	5.28	0.12

* The results of the measurements of the dipole moments of the substances marked with an asterisk, have been presented previously by us [1].

LITERATURE CITED

- [1] Z. V. Pushkareva and Z. Yu. Kokoshko, Proc. Acad. Sci. USSR, 93, 77(1953).
 [2] Z. V. Pushkareva and Z. Yu. Kokoshko, J. Gen. Chem., 24, 874 (1954). *
 [3] Hodestrand, Z. phys. Chem 2, 428 (1929).

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* Translation page 869, this issue.

DIALKYL ESTERS OF ARYLSULFONAMIDOPHOSPHORIC ACIDS

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Dialkyl esters of arylsulfonamidophosphoric acids were obtained by the acidic or alkaline hydrolysis of the trialkyl esters of arylsulfonamidophosphoric acids, and directly from trichlorophosphazonesulfonaryls by the action of excess of sodium alcoholates [1]. The preparation of the dialkyl esters of arylsulfonamidophosphoric acids by the action of sodium alcoholates on the di-(acid chlorides) of arylsulfonamidophosphoric acids, which completely and rigorously demonstrates the structure of these esters, is described in the present work.

In comparison with trichlorophosphazonesulfonaryls, the di-(acid chlorides) of arylsulfonamidophosphoric acids react considerably less energetically with sodium alcoholates. When the di-(acid chloride) of an arylsulfonamidophosphoric acid, ground to a fine powder, is added to a solution of sodium alcoholate in the corresponding alcohol, the reaction proceeds smoothly with insignificant evolution of heat. The sodium salts of the dialkyl esters are formed in excellent yields as a result of the reaction according to the scheme:



The formulas, yields, and melting points of the dialkyl esters of arylsulfonamidophosphoric acids thus obtained are presented in Table 1.

The dimethyl and diethyl esters crystallize well and are readily isolated from the reaction mixture in the pure state. The dibutyl esters consist of thick, viscous liquids, difficult to purify as such; therefore they were isolated and purified in the form of the characteristic sodium salts, by the decomposition of which the pure dibutyl esters were obtained.

TABLE 1

Number of the ester	Formula of the dialkyl ester	Yield (%)	M.p.
1	$\text{C}_6\text{H}_5\text{SO}_2\text{NHPO}(\text{OCH}_3)_2$	84.1	108-109*
2	$\text{o-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHPO}(\text{OCH}_3)_2$	86.3	145-146
3	$\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHPO}(\text{OCH}_3)_2$	74.8	110-111
4	$\alpha\text{-C}_{10}\text{H}_7\text{SO}_2\text{NHPO}(\text{OCH}_3)_2$	75.2	164-165
5	$\text{C}_6\text{H}_5\text{SO}_2\text{NHPO}(\text{OC}_2\text{H}_5)_2$	80.1	111-112
6	$\text{o-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHPO}(\text{OC}_2\text{H}_5)_2$	83.3	97-98
7	$\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHPO}(\text{OC}_2\text{H}_5)_2$	78.6	105-106
8	$\alpha\text{-C}_{10}\text{H}_7\text{SO}_2\text{NHPO}(\text{OC}_2\text{H}_5)_2$	69.0	154-155
9	$\beta\text{-C}_{10}\text{H}_7\text{SO}_2\text{NHPO}(\text{OC}_2\text{H}_5)_2$	79.1	161-162
10	$\text{C}_6\text{H}_5\text{SO}_2\text{NHPO}(\text{OC}_4\text{H}_9\text{-n})_2$	90.2*	liquid
11	$\text{o-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHPO}(\text{OC}_4\text{H}_9\text{-n})_2$	88.7*	liquid
12	$\alpha\text{-C}_{10}\text{H}_7\text{SO}_2\text{NHPO}(\text{OC}_4\text{H}_9\text{-n})_2$	91.8*	75-77
13	$\beta\text{-C}_{10}\text{H}_7\text{SO}_2\text{NHPO}(\text{OC}_4\text{H}_9\text{-n})_2$	90.4*	liquid

* In the form of the sodium salts.

The dialkyl esters of the arylsulfonamidophosphoric acids, obtained from their corresponding di-(acid chlorides) can be distinguished neither in their physical, nor in their chemical properties from the dialkyl esters obtained by other methods [1]. The sodium salts of dimethyl and diethyl esters of arylsulfonamidophosphoric acids are readily soluble in water and alcohol and insoluble in nonpolar solvents. The sodium salts of the dibutyl esters of arylsulfonamidophosphoric acids are not only soluble in water and alcohol, but also in nonpolar solvents, for example, in benzene, ether and hot carbon tetrachloride and, with more difficulty, in petroleum ether. The sodium salts of the dibutyl esters are salted out from aqueous solutions even by small concentrations of sodium chloride.

The sodium salt of the dibutyl ester of α -naphthylsulfonamidophosphoric acid is somewhat different in its solubility. It readily dissolves only in hot benzene, is difficultly soluble in cold benzene and very difficultly soluble in carbon tetrachloride and

in petroleum ether. Only 0.76 g of the salt dissolves at 20° in 100 ml of benzene. The sodium salts of the dibutyl esters of the other arylsulfonamidophosphoric acids are considerably more soluble in benzene.

The sodium salts of the dibutyl esters crystallize well from a mixture of benzene with petroleum ether (1:1) in the form of fine, long needles. They have comparatively low melting points (from 145 to 190°) and melt sharply in ranges of 2-3°. The sodium salts of the dibutyl esters, as well as the free esters, have an extraordinarily bitter taste.

See the experimental part relative to the hydrolysis of the dialkyl esters with hydrochloric acid in water-alcohol solutions.

The di-(acid chlorides) of the arylsulfonamidophosphoric acids have been described in the literature [2] as crystalline substances which do not have sharp melting points and begin to melt at around 110°. Actually, twice recrystallized di-(acid chlorides) when heated in a capillary, begin to melt at around 110° and do not have a sharp melting point. However, when the di-(acid chlorides) are subjected to several recrystallizations from benzene and then from carbon tetrachloride, substances are obtained with sharp melting points. The di-(acid chloride) of phenylsulfonamidophosphoric acid which has been purified in this way melts at 132-133° without decomposition; it is of interest to note that the substance, melting at 132-133°, and the substance which begins to decompose at 110°, do not differ from each other either in their external form nor in their analytical data. Evidently, there is a negligible quantity of admixture which is difficult to eliminate by crystallization and does not influence the analytical results, but causes a marked lowering of the melting point.

The di-(acid chloride) of β -naphthylsulfonamidophosphoric acid, which has not been described in the literature, was prepared similarly to the other di-(acid chlorides) of this type by the reaction of trichlorophosphazone-sulfon- β -naphthyl with formic acid in accordance with a method described in the literature [2]. In contrast to the di-(acid chlorides) of phenyl-, o-tolyl-, p-tolyl-, and α -naphthylsulfonamidophosphoric acids, the di-(acid chloride) of β -naphthyl-sulfonamidophosphoric acid is readily soluble in benzene.

EXPERIMENTAL

Reaction of di-(acid chlorides) of arylsulfonamidophosphoric acids with a solution of sodium methylate in methyl alcohol.

0.01 mole of the di-(acid chloride) of the arylsulfonamidophosphoric acid, carefully ground into a fine powder, was added to a solution of 0.03 g-atoms of metallic sodium (0.7 g) in 15 ml of anhydrous methyl alcohol which was cooled with running water and was being energetically stirred.

When all the di-(acid chloride) had reacted, the sodium chloride was drawn off, washed with a small quantity of methyl alcohol, and the filtrate was concentrated to dryness in a vacuum. 10 ml of 2 N H_2SO_4 was added to the dry residue and the mixture well stirred to isolate the dimethyl esters of the arylsulfonamidophosphoric acids.

The dimethyl esters precipitated either in the form of fine, well formed crystals, or in the form of a thick oily layer which, when rubbed with a glass rod, was converted into a crystalline mass. The crystalline powder was separated, washed several times with small portions of water, and dried. The melting point of the dimethyl esters thus obtained differs from the melting point of the recrystallized products by only 2-3°. A single subsequent crystallization usually gave a pure ester with a sharp melting point.

The following dimethyl esters of arylsulfonamidophosphoric acids were thus obtained. *

1. Dimethyl ester of phenylsulfonamidophosphoric acid, yield 2.23 g.

Found %: OCH_3 23.46. Equiv. ** 1.02. Calculated %: OCH_3 23.41. Equiv. 1.00.

2. Dimethyl ester of o-tolylsulfonamidophosphoric acid, yield 2.41 g.

Found %: OCH_3 22.08. Equiv. ** 1.01. Calculated %: OCH_3 22.22. Equiv. 1.00.

3. Dimethyl ester of p-tolylsulfonamidophosphoric acid, yield 2.09 g.

Found %: OCH_3 22.12. Equiv. ** 1.00. Calculated %: OCH_3 22.22. Equiv. 1.00.

4. Dimethyl ester of α -naphthylsulfonamidophosphoric acid, yield 2.37 g.

Found %: OCH_3 19.61. Equiv. ** 1.02. Calculated %: OCH_3 19.69. Equiv. 1.00

A mixed sample of the dimethyl esters obtained with dimethyl esters of the arylsulfonamidophosphoric acids, obtained by other methods [1], displayed no melting point depression.

Reaction of the di-(acid chlorides) of arylsulfonamidophosphoric acids with a solution of sodium ethylate in ethyl alcohol.

The reaction of the di-(acid chlorides) of the arylsulfonamidophosphoric acids with a solution of sodium

* For the formulas, yields (in %) and melting points of the esters, see Table 1.

** The indicator was phenolphthalein.

ethylate was carried out in the same way as the reaction with sodium methylate.

The following diethyl esters of arylsulfonamidophosphoric acids were prepared.

5. Diethyl ester of phenylsulfonamidophosphoric acid, yield 2.23 g.

Found %: OC_2H_5 30.62. Equiv. $\cdot\cdot$ 1.07. Calculated %: OC_2H_5 30.72. Equiv. 1.00

6. Diethyl ester of o-tolylsulfonamidophosphoric acid, yield 2.56 g.

Found %: OC_2H_5 29.29. Equiv. $\cdot\cdot$ 1.03. Calculated %: OC_2H_5 29.33. Equiv. 1.00

7. Diethyl ester of p-tolylsulfonamidophosphoric acid, yield 2.41 g.

Found %: OC_2H_5 29.22. Equiv. $\cdot\cdot$ 1.01. Calculated %: OC_2H_5 29.33. Equiv. 1.00

8. Diethyl ester of α -naphthylsulfonamidophosphoric acid, yield 2.37 g.

Found α : OC_2H_5 26.32. Equiv. $\cdot\cdot$ 1.02. Calculated %: OC_2H_5 26.32. Equiv. 1.00.

9. Diethyl ester of β -naphthylsulfonamidophosphoric acid, yield 2.71 g.

Mixed samples of the diethyl esters obtained, with the diethyl esters of arylsulfonamidophosphoric acids obtained by other methods [1], displayed no melting point depression.

Reaction of the di-(acid chlorides) of arylsulfonamidophosphoric acids with a solution of sodium n-butylate in butyl alcohol

0.01 mole of the di-(acid chloride) of the arylsulfonamidophosphoric acid, carefully ground into a fine powder, was added to a solution of 0.03 g-atom of metallic sodium (0.7 g) in 20 ml of anhydrous butyl alcohol at room temperature and while it was being energetically stirred. The reaction proceeded with insignificant evolution of heat. To complete the reaction, the mixture was heated for 30 minutes on a boiling water bath. The butyl alcohol was then distilled off in a vacuum on a water bath; 10 ml of water was added to the dry residue, and the mixture obtained was transferred to a separatory funnel, energetically extracted, and let stand. The sodium salts of the dibutyl esters were readily soluble in water; however in the presence of even comparatively small quantities of sodium chloride, the solution readily separated into 2 layers. The lower layer consisted of an aqueous solution, chiefly of the sodium salt of the dibutyl ester; the upper layer consisted of an aqueous solution of sodium chloride. The lower layer was poured out into a small porcelain dish and dried on a water bath. A colorless crystalline mass of the sodium salt of the dibutyl ester with a small admixture of sodium chloride was obtained in the residue.

The sodium salts of the dibutyl esters were readily obtained in the pure form by crystallization from a mixture of equal volumes of petroleum ether (b.p. 95-100°) and benzene. See the general section for the properties of the sodium salts.

The reaction of the di-(acid chlorides) of the arylsulfonamidophosphoric acids with sodium butylate was accompanied by the formation of a small quantity of by-products which had an extraordinarily unpleasant odor.

The following sodium salts were obtained:

The sodium salt of the di-n-butyl ester of phenylsulfonamidophosphoric acid was obtained in a yield of 3.35 g (90.2%). It consisted of long, fine, transparent needles, m.p. 145-147°.

0.5901 g sub.: 0.1133 g Na_2SO_4 . 0.3667 g sub.: 0.0695 g Na_2SO_4 . Found %: Na 6.22, 6.14. $\text{C}_{14}\text{H}_{23}\text{O}_5\text{NSPNa}$. Calculated %: Na 6.19.

The sodium salt of the di-n-butyl ester of o-tolylsulfonamidophosphoric acid was obtained in a yield of 3.42 g (88.7%). It consisted of long, fine, transparent prisms, m.p. 153-157°.

0.5091 g sub.: 0.0888 g Na_2SO_4 . 0.4362 g sub.: 0.0798 g Na_2SO_4 . Found %: Na 5.65, 5.92. $\text{C}_{15}\text{H}_{25}\text{O}_5\text{NSPNa}$. Calculated %: Na 5.97.

The sodium salt of the di-n-butyl ester of α -naphthylsulfonamidophosphoric acid was obtained in a yield of 3.87 g (91.8 %). The salt was very readily soluble in water, alcohol and acetone, comparatively readily soluble in hot benzene, and more poorly soluble in cold benzene. 0.76 g of the salt dissolved in 100 ml of benzene at 20°. It was difficultly soluble in ether and very difficultly soluble in petroleum ether and carbon tetrachloride. It precipitated from benzene in the form of a flocculent precipitate, which consisted of an aggregate of very minute, transparent, thin prisms, m.p. 187-189°.

0.4707 g sub.: 0.0779 g Na_2SO_4 . 0.4833 g sub.: 0.0788 g Na_2SO_4 . Found %: Na 5.36, 5.28. $\text{C}_{18}\text{H}_{25}\text{O}_5\text{NSPNa}$. Calculated %: Na 5.46.

The sodium salt of the di-n-butyl ester of β -naphthylsulfonamidophosphoric acid was obtained in a yield of 3.81 g (90.4 %). In contrast to the sodium salt of α -naphthyl-sulfonamidophosphoric acid, the sodium salt of the β -naphthylsulfonamidophosphoric acid was very readily soluble in benzene. It crystallized from a mixture of benzene and petroleum ether in the form of well formed prisms, m.p. 175-180°.

0.3891 g sub.: 0.0639 g Na_2SO_4 . 0.4006 g sub.: 0.0668 g Na_2SO_4 . Found %: Na 5.32, 5.40. $\text{C}_{18}\text{H}_{25}\text{O}_5\text{NSPNa}$. Calculated %: Na 5.46.

Preparation of the di-n-butyl esters of arylsulfonamidophosphoric acids.

0.01 mole of the sodium salt of arylsulfonamidophosphoric acid was dissolved in 30 ml of water and the solution was acidified with 15.0 ml of 2 N H_2SO_4 . The viscous oily layer which separated out was washed with water and dissolved in ether. The ethereal solution was washed with water, dried with anhydrous sodium sulfate and the solvent driven off in a vacuum on a water bath. A colorless or slightly yellowish thick viscous oil was obtained in the residue. It consisted exclusively of the dibutyl ester of α -naphthylsulfonamidophosphoric acid, which readily crystallized.

The following esters were obtained in this manner:

10. Di-n-butyl ester of phenylsulfonamidophosphoric acid, yield 3.25 g (93.0 %). It consisted of a thick, viscous oil.

0.0404 g sub.: 1.365 ml N_2 (18°, 742 mm). 0.2741 g sub.: 3.90 ml 0.2046 N NaOH. 0.6401 g sub.: 9.45 ml 0.2046 N NaOH. Found %: N 3.87. Equiv. 1.02, 1.06. $\text{C}_{14}\text{H}_{24}\text{O}_5\text{NSP}$. Calculated %: N 4.01. Equiv. 1.00.

11. Di-n-butyl ester of o-tolylsulfonamidophosphoric acid, yield 3.42 g (99.1%). It consisted of a thick viscous liquid.

0.0356 g sub.: 1.120 ml N_2 (18°, 742 mm). 0.4876 g sub.: 6.85 ml 0.2046 N NaOH. 0.7003 g sub.: 9.55 ml 0.2046 N NaOH. Found %: N 3.60. Equiv. 1.04, 1.01. $\text{C}_{15}\text{H}_{20}\text{O}_5\text{NSP}$. Calculated %: N 3.60. Equiv. 1.00.

12. Di-n-butyl ester of α -naphthylsulfonamidophosphoric acid, yield 3.59 g (89.9 %). It crystallized from petroleum ether (b.p. 95-100°) in the form of fine, well formed prisms with a m.p. of 75-77°.

0.0364 g sub.: 0.0723 g CO_2 ; 0.0219 g H_2O . 0.3125 g sub.: 3.90 ml 0.2046 N NaOH. Found %: C 54.23; H 6.72. Equiv. 1.02. $\text{C}_{19}\text{H}_{20}\text{O}_5\text{NSP}$. Calculated %: C 54.14; H 6.56. Equiv. 1.00.

13. Di-n-butyl ester of β -naphthylsulfonamidophosphoric acid, yield 3.43 g (85.9%). It consisted of a thick, viscous liquid.

0.5433 g sub.: 6.30 ml 0.2046 N NaOH. 0.5027 g sub.: 6.42 ml 0.2046 N NaOH. Found: Equiv. 1.00 1.04. $\text{C}_{19}\text{H}_{20}\text{O}_5\text{NSP}$. Calculated: Equiv. 1.00.

The di-n-butyl esters of arylsulfonamidophosphoric acids were very readily soluble in alcohol, ether, acetone, benzene and carbon tetrachloride. The dibutyl esters were insoluble in water and cold petroleum ether.

TABLE 2

Formula of the ester, subjected to hydrolysis	Quantity of un- hydrolyzed ester		Yield of the amide of the arylsulfonic acid		Total yield (% in %)
	(In g)	(In %)	(In g)	(In %)	
$\text{C}_6\text{H}_5\text{SO}_2\text{NHP}(\text{OCH}_2)_2$	0	0	0.28	89.2	89.2
$\alpha\text{-C}_{10}\text{H}_7\text{SO}_2\text{NHP}(\text{OCH}_2)_2$	0.03	4.8	0.32	77.2	82.0
$\text{C}_8\text{H}_5\text{SO}_2\text{NHP}(\text{OC}_2\text{H}_5)_2$	0.08	13.6	0.17	54.2	67.8
$\alpha\text{-C}_{10}\text{H}_7\text{SO}_2\text{NHP}(\text{OC}_2\text{H}_5)_2$	0.15	21.8	0.23	55.5	77.3

Hydrolysis of the dimethyl and diethyl esters of the arylsulfonamidophosphoric acids by a water-alcohol solution of hydrochloric acid.

A mixture of 0.002 mole of the dialkyl ester of the arylsulfonamidophosphoric acid with 20 ml of a 1 N water-alcohol solution of hydrochloric acid (10 ml of 2 N aqueous solution of the acid + 10 ml of alcohol) was boiled with a reflux condenser for 24 hours. To separate the hydrolysis products, the alcohol was driven off in a vacuum and the residue was neutralized with a solution of sodium hydroxide (to a neutral reaction to phenolphthalein). The insoluble sulfamides were separated, washed with water, dried and weighed. After separating the amide, the filtrate was concentrated in a vacuum to a volume of about 5 ml and acidified with several drops of concentrated hydrochloric acid. The dimethyl and diethyl esters which had not hydrolyzed thereupon precipitated in the form of an oil which readily crystallized. The dialkyl esters were separated, washed, dried and weighed. The amides of the arylsulfonic acids and the dialkyl esters of the arylsulfonamidophosphoric acids were identified by the melting point.

The yields of hydrolysis products are presented in Table 2.

SUMMARY

1. A method for preparing the dialkyl esters of arylsulfonamidophosphoric acids from the di-(acid chlorides) of these acids and sodium alcoholates was described.
2. The dimethyl, diethyl and di-n-butyl esters of the arylsulfonamidophosphoric acids and the sodium salts of the di-n-butyl esters were prepared, and their properties were described.

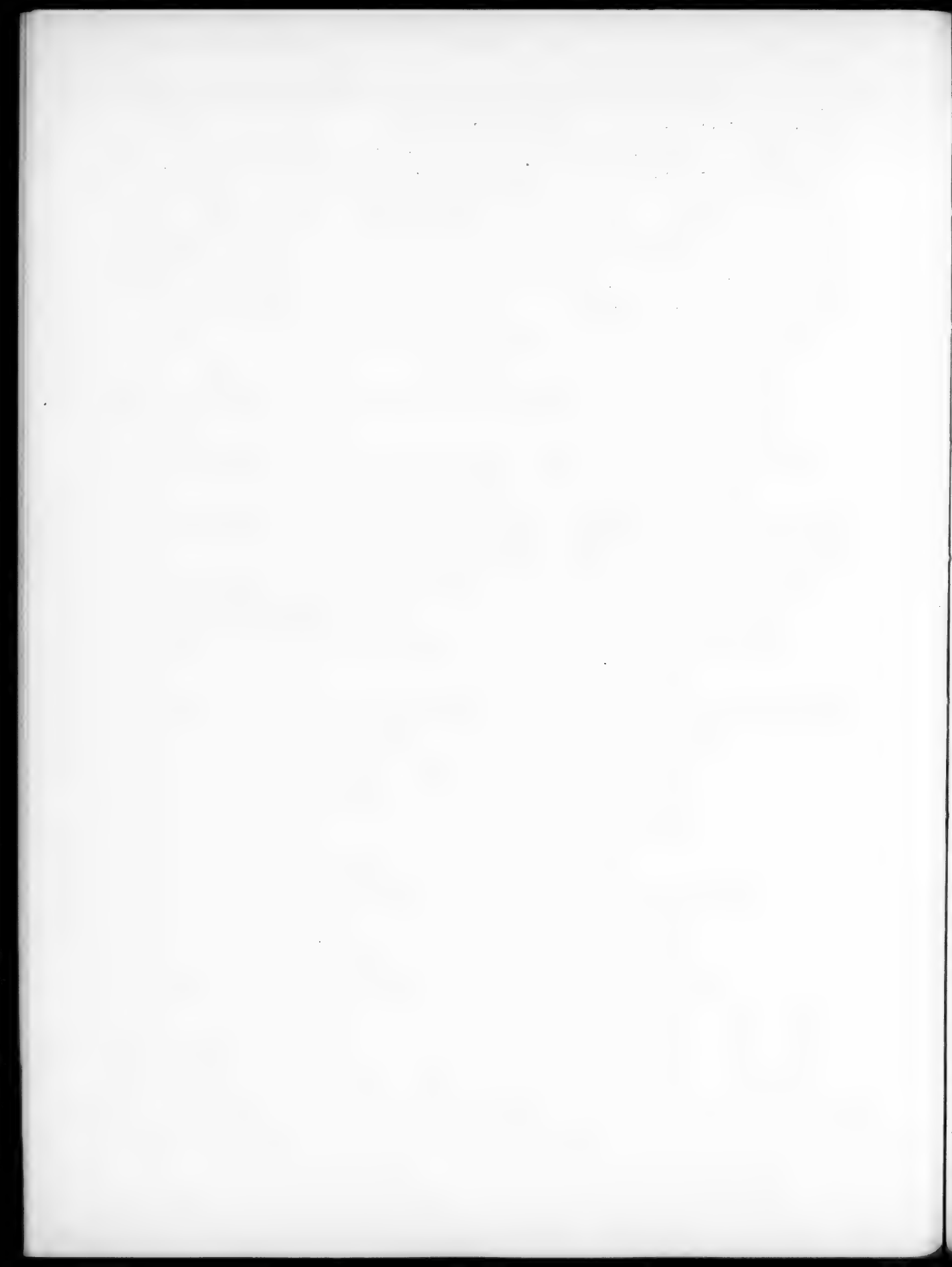
LITERATURE CITED

- [1] A. V. Kirsanov and V. I. Shevchenko, J. Gen. Chem., 24, 474 (1954). *
- [2] A. V. Kirsanov and E. A. Abrazhanova, J. Gen. Chem., Supp. II, 1048 (1953).

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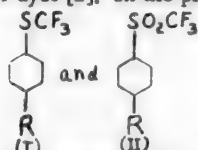
* See Consultants Bureau Translation, p. 483.



PHENYLTRIFLUOROMETHYLSULFIDES AND PHENYLTRIFLUOROMETHYSULFONES WITH SUBSTITUENTS IN THE PARA POSITION

L. M. Yagupolsky and M. S. Marenets

Aromatic compounds which contain the SCF_3 and SO_2CF_3 groups have been only slightly studied [1,2]. In spite of this, they, analogously to other aromatic compounds which contain SAlk and SO_2Alk groups as substituents, may be of interest as physiologically active substances [3], insecticides [1] and intermediate products for the synthesis of dyes [2]. In the present work, we have synthesized a series of compounds of the type:





where $\text{R} = \text{Br, I, CN, COOH, COOC}_2\text{H}_5, \text{CONH}_2, \text{NH}_2^* \text{ and } \text{NHCOCH}_3^*.$

The substances containing the SCF_3 group were prepared by us via the chlorination of the methyl group in the p-nitrophenylmethylsulfide and replacement of the chlorine atoms in it by fluorine with the aid of antimony trifluoride. The p-nitrophenyl-trifluoromethylsulfide was reduced into the amine [2]. The amino group was replaced with other substituents by the Sandmeyer reaction.

SCF_3 derivatives differ in their physical properties from the corresponding SCH_3 derivatives. Replacement of the methyl group by the trifluoromethyl group, as in many other cases, lowers the boiling point of the compound. The specific gravity of the preparations with the SCF_3 substituent is higher than the specific gravity of the corresponding compounds with the SCH_3 group. Trifluoromethylmercapto derivatives melt lower in the majority of cases than substances which contain methylmercapto groups.

In the table we present the physical properties of compounds with the general formula (I) and, for comparison, the data on the physical properties of the corresponding para-substituted methylphenylsulfides which are presented in the literature.

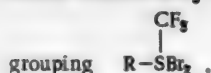
R	R-  -SCF ₃			R-  -SCH ₃		
	Temperature		Specific gravity	Temperature		Specific gravity
	M.p.	B.p.		M.p.	B.p.	
H	—	141-142° [1]	d_4^{20} 1.2661	—	189-190° [4]	d_4^{20} 1.0576 [5]
Br	—	190-191	d_4^{22} 1.6463	37° [4]	255 [4]	d_4^{20} 1.4584 [5]
I	—	86-87 at 10 mm	d_4^{22} 1.8677	38 [6]	—	—
OH	57-58°	—	—	84-85 [7]	—	—
CN	40-41	—	—	64 [6]	—	—
COOH	160-161	—	—	192 [6]	—	—
COOC ₂ H ₅	—	96-97 at 5 mm	d_4^{25} 1.2752	28 [8]	168 [8] at 15 mm	—

The trifluoromethylmercapto group is stable and resistant to the action of acids and alkalis. Thus, when p-cyanophenyltrifluoromethylsulfide is saponified with concentrated hydrochloric acid in a sealed tube at 130-140° for 6 hours, the SCF_3 group is not decomposed.

In contrast to the CF_3 group in p-hydroxybenzotrifluoride [9], the SCF_3 group in p-hydroxyphenyltrifluoromethylsulfide is not changed by the action of a 2 N solution of alkali in the cold or upon heating.

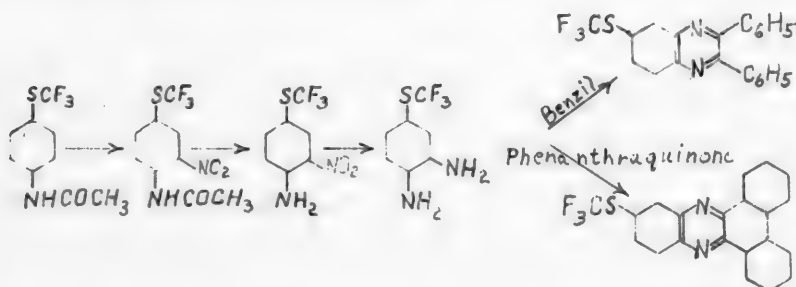
* The p-amino- and p-acetylaminophenyltrifluoromethylsulfides were described by one of us and A. I. Kiprianov in a previous work [2].

In the SCF_3 radical, the electrons are drawn off from the sulfur atom by the electronegative trifluoromethyl group. This, apparently, explains the fact that, in contrast to phenylmethylsulfide and its derivatives, compounds which contain SCF_3 as a substituent do not add molecules of chlorine or bromine with the formation of the stable



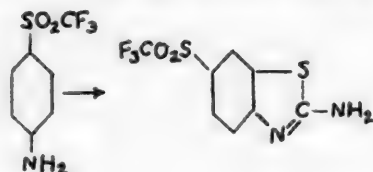
This same fact probably also explains why p-nitrophenylmethylsulfide dissolves in concentrated sulfuric acid with the formation of a reddish-violet solution [10], while p-nitrophenyltrifluoromethylsulfide gives a yellow colored solution when dissolved in concentrated sulfuric acid.

p-Acetylaminophenyltrifluoromethylsulfide was treated with a nitrating mixture; under these conditions the nitro group was located in the ortho position to the acetyl amino group. After saponification of the acetyl group and reduction of the nitroamine into diamine, the latter, like all o-phenylenediamines, forms the corresponding derivatives of quinoxaline and phenanthrazine with benzil and phenanthraquinone:



The compounds containing the SO_2CF_3 group were prepared by oxidizing p-nitrophenyltrifluoromethylsulfide with chrome mixture, reducing the nitro group into the amino group and replacing it, by the Sandmeyer reaction, with other substituents. The SO_2CF_3 group is less resistant to the action of alkalis than the SCF_3 group. Thus, when p-hydroxyphenyltrifluoromethylsulfone is boiled for 5 minutes with dilute or concentrated alkali, the fluoride ion is detected in the solution.

2-Amino-6-trifluoromethylbenzthiazolylsulfone was obtained by the rhodanization of p-aminophenyltrifluoromethylsulfone:



EXPERIMENTAL

Phenyltrichloromethylsulfide

40 g of methylphenylsulfide was dissolved in 120 g of dry chloroform, and dry chlorine was passed through the solution while it was being cooled with ice water and illuminated with a lamp (200 W). During a period of 20 minutes, chlorine was absorbed and hydrogen chloride was not evolved. Then an abundant evolution of hydrogen chloride began. The chlorination was continued until the calculated increase in weight was obtained and then the solution was left for 1 hour at room temperature. The chloroform was distilled off. The product was vacuum distilled. The b.p. was 108–110° at 5 mm. The m.p. was 35°. The yield was 66 g (90%).

Found %: Cl 46.63, 46.73. $\text{C}_7\text{H}_5\text{SCl}_3$. Calculated %: Cl 46.79

Phenyltrifluoromethylsulfide

32 g of phenyltrichloromethylsulfide and 32 g of sublimed antimony trifluoride were rapidly heated in a Wurtz flask until the exothermic reaction began. The phenyltrifluoromethylsulfide which formed was distilled off. The product was extracted with ether and the ethereal solution was washed with 6 N HCl and then with water and was dried. The product distilled at 140–142° (in accord with the melting point of this compound, set forth in the patent [1]), n_D^{25} 1.4619. The yield was 17.5 g (70%).

p-Aminophenyltrifluoromethylsulfide was prepared by reducing the corresponding nitro derivative [2].

p-Bromophenyltrifluoromethylsulfide. a) 5.8 g of p-aminophenyltrifluoromethylsulfide was diazotized, and the amino group was replaced with bromine in the usual way by Sandmeyer's method. The yield of a product with b.p. 190-191°, n_D^{20} 1.5126 was 4 g (52%).

Found %: S 12.70, 12.76. $C_7H_4SBrF_3$. Calculated %: S 12.46.

b) the p-bromophenyltrifluoromethylsulfide was also prepared from p-bromophenylmethylsulfide via chlorination of the methyl group and replacement of the chlorine atoms with fluorine with the aid of SbF_3 .

9.1 g of p-bromophenylmethylsulfide [11] was dissolved in 45 ml of dry chloroform, and dry chlorine was passed through the solution for 1 hour. The flask was cooled with ice water. The mixture was let stand for 1 hour, at room temperature. The chloroform was distilled off. The yield of p-bromophenyltrichloromethylsulfide was quantitative—13.6 g. After crystallization from alcohol, the product melted at 78°.

Found %: S 10.39, 10.12. $C_7H_4SCl_3Br$. Calculated %: S 10.44

6.5 g of p-bromophenyltrichloromethylsulfide and 5 g of sublimed antimony trifluoride were quickly heated to boiling in a Wurtz flask. The product was distilled, extracted with ether, the ethereal solution washed with 6 N HCl, then with water, and was dried. The ether was distilled off. The product distilled at 190-191°, n_D^{20} 1.5126. The yield was 4.2 g (77.7%).

p-Iodophenyltrifluoromethylsulfide

5 g of p-aminophenyltrifluoromethylsulfide was diazotized and the amino group replaced with iodine by the Sandmeyer reaction. The yield of product was 4.3 g (55%). The b.p. was 86-87° at 10 mm, n_D^{17} 1.5588.

Found %: S 10.56, 10.80. $C_7H_4SF_3I$. Calculated %: S 10.52.

p-Hydroxyphenyltrifluoromethylsulfide

7 g of p-aminophenyltrifluoromethylsulfide was diazotized in a sulfuric acid solution. The mixture was stirred for 1 hour at room temperature until the precipitate of amine salt disappeared. The solution of diazonium salt was slowly added from a dropping funnel into a steam distillation flask. The diazonium salt was decomposed, and the phenol was simultaneously steam distilled. The distillate was saturated with sodium chloride. The phenol was extracted with ether. The ether was distilled off. The product was vacuum distilled. The b.p. was 77-78° at 7 mm, and the m.p. 57-58°. The yield was 4.9 g (70%).

Found %: S 16.47, 16.68. $C_7H_5OSF_3$. Calculated % S 16.5

The p-nitrobenzoyl derivative of the phenol melted at 81-82°.

Found %: S 9.40, 9.51. $C_{14}H_9O_4NSF_3$. Calculated %: S 9.33.

3,5-Dibromo-4-hydroxyphenyltrifluoromethylsulfide was prepared by adding bromine to a solution of the phenol in acetic acid. The solution was left overnight. The needles which precipitated were filtered and crystallized from acetic acid. The m.p. was 54-55°. The product can also be purified by sublimation.

Found %: S 8.91, 8.99. $C_7H_3OBr_2SF_3$. Calculated %: S 9.09.

p-Cyanophenyltrifluoromethylsulfide

10 g of p-aminophenyltrifluoromethylsulfide was diazotized and the amino group replaced with the nitrile group in the usual way, by Sandmeyer's method. After completion of the decomposition of the cyanide complex of the diazonium salt, the product was steam distilled and extracted from the distillate with ether. The ethereal solution was washed with 2 N sodium hydroxide and then with water. The ether was distilled off. The product was shaken with a hydrochloric acid solution of stannous dichloride. The nitrile was separated, washed with water and extracted with ether. The ethereal solution was dried, washed with alkali and water, and the ether distilled off. The product was vacuum distilled. The b.p. was 89-90° at 10 mm. After crystallization from low-boiling petroleum ether, the m.p. was 40-41°. The yield was 4.4 g (42%).

Found %: N 7.0, 7.13. $C_8H_4NSF_3$. Calculated %: N 6.9.

p-Carboxyphenyltrifluoromethylsulfide

2.4 g of p-cyanophenyltrifluoromethylsulfide was sealed in a tube with 6 ml of concentrated hydrochloric acid and heated for 6 hours at a temperature of 130-140°. After opening the tube, the product was filtered and dissolved in alkali. The alkaline solution was filtered, and the p-carboxyphenyltrifluoromethylsulfide was precipitated with hydrochloric acid. The yield was 2.26 g (83%). After crystallization from aqueous alcohol, the m.p. was 160-161°.

Found %: S 14.54, 14.61. Equiv. 220. $C_8H_5O_2SF_3$. Calculated %: S 14.42, Equiv. 221.

The acid chloride of the acid.

Obtained by heating 3 g of the acid on a water bath with a 5-fold excess of thionyl chloride for 3 hours. The thionyl chloride was distilled off. The product was vacuum distilled. The b.p. was 104-105° at 12 mm. The yield was 3 g (92%).

The ethyl ester of p-carboxyphenyltrifluoromethylsulfide;

Prepared by heating 2.4 g of the acid chloride of the acid on a water bath with 10 ml of anhydrous ethyl alcohol. The alcohol was distilled off. The product was vacuum distilled. A liquid with a pleasant odor was obtained. The b.p. was 96-97° at 5 mm, n_D^{25} 1.4812. The yield was 2.2 g (88%).

The hydrazide of the acid

Prepared by boiling the ethyl ester of the acid with hydrazine hydrate. After crystallization from aqueous alcohol, the m.p. was 124-125°

Found %: N 12.12, 12.16. $C_8H_7ON_2SF_3$. Calculated %: N 11.86.

The amide of the acid.

Prepared from the acid chloride of the acid and aqueous ammonia. The amide was crystallized from aqueous alcohol. The m.p. was 125-126°.

Found %: N 6.44, 6.49. $C_8H_6ONSF_3$. Calculated %: N 6.34.

3-Nitro-4-acetylaminophenyltrifluoromethylsulfide.

3.6 g of p-acetylaminophenyltrifluoromethylsulfide was placed in a three-necked flask, equipped with a mechanical stirrer, a thermometer and a dropping funnel. A nitrating mixture (6 ml of HNO_3 , d 1.41, and 7 ml of H_2SO_4 , d 1.84), cooled to -5°, was slowly added to the acetyl derivative. The mixture was stirred for 2 hours. During and after the addition of the nitrating mixture, the temperature was kept at 2-4°. The product was poured out on ice, filtered and washed with water. The yield of crude product was 4.2 g. After crystallization from alcohol, 3.7 g (86%) of long yellow needles with a m.p. of 101-102° was obtained.

Found %: N 10.08, 9.9. $C_9H_7O_3N_2SF_3$. Calculated %: N 10.00.

3-Nitro-4-aminophenyltrifluoromethylsulfide.

3.6 g of 3-nitro-4-acetylaminophenyltrifluoromethylsulfide was boiled on a water bath with a solution of 1.2 g of potassium hydroxide in 10 ml of 75% alcohol for 15 minutes. The mixture was left overnight. The solution was diluted with water, and the product filtered and washed with water. The yield was 2.9 g (95%). After crystallization from alcohol, the m.p. was 85-86°.

Found %: N 11.82, 11.90. $C_7H_5O_2N_2SF_3$. Calculated %: N 11.76

3,4-Diaminophenyltrifluoromethylsulfide.

A solution of 10 g of stannous dichloride in 40 ml of concentrated hydrochloric acid was gradually added to a solution of 3 g of 3-nitro-4-aminophenyltrifluoromethylsulfide in 25 ml of alcohol. The temperature was kept at 50-60°. The solution was then heated for 1 hour on a water bath. The alcohol was distilled off under the vacuum created by a water jet pump. The residue was rendered alkaline with a solution of sodium hydroxide. The product was extracted with ether. The ethereal solution was dried. The ether was distilled off. The yield was 1.9 g (75%). After crystallization from aqueous alcohol, it consisted of white needles with a m.p. of 46-47°.

Found %: N 13.62, 13.69. $C_7H_7N_2SF_3$. Calculated %: N 13.46.

The diacetyl derivative

Prepared from the diamine and acetic anhydride. After crystallization from alcohol, the m.p. was 190-191°.

Found %: N 9.36, 9.49. $C_{11}H_{11}O_4N_2SF_3$. Calculated %: N 9.58.

2,3-Diphenyl-6-trifluoromethylmercaptoquinoxaline.

0.2 g of 3,4-diaminophenyltrifluoromethylsulfide and 0.2 g of benzil were dissolved in alcohol and heated on a water bath. After dilution with water, the product was filtered and crystallized from aqueous alcohol. The m.p. was 140-141°. The yield was 0.25 g (66%).

Found %: N 7.48, 7.36. $C_{21}H_{13}N_2SF_3$. Calculated %: N 7.33.

2-Trifluoromethylmercaptophenanthrazine.

A solution of 0.2 g of 3,4-diaminophenyltrifluoromethylsulfide in 7 ml of alcohol was added to a warm solution of 0.2 g of phenanthraquinone in 20 ml of glacial acetic acid. After several minutes, the reaction product precipitated. The yield was 0.25 g (66%). The m.p. was 200-201°. After crystallization from alcohol, the melting point did not change.

Found %: N 7.23, 7.38. $C_{21}H_{11}N_2SF_3$. Calculated %: N 7.36.

p-Nitrophenyltrifluoromethylsulfone.

44.6 g of p-nitrophenylmethylsulfide, 28 g of CrO_3 , 28 ml of H_2SO_4 and 35 ml of water were placed in a reaction vessel equipped with a mechanical stirrer, a thermometer and a reflux condenser. The mixture was stirred for 15 hours at a temperature of 120-130°. The product was steam distilled and filtered. 44.8 g of the sulfone was obtained. After crystallization from 200 ml of alcohol, the yield amounted to 41.5 g (81.3%). The m.p. of 85-86° was in accord with that set forth in the patent [1].

p-Aminophenyltrifluoromethylsulfone.

To a solution of 33 g of p-nitrophenyltrifluoromethylsulfone in 150 ml of alcohol, a solution of 120 g of $SnCl_2$ in 150 ml of concentrated hydrochloric acid was gradually added at such a rate that the temperature did not rise above 60°. The mixture was then heated for 1 hour on a water bath. The alcohol was distilled off under a water jet pump vacuum. The solution was poured out on a mixture of ice and 40% NaOH solution. The amine was extracted with ether. The ether was distilled off. The product was crystallized from alcohol. The m.p. was 96-97°. The yield was 26 g (89.3%).

Found %: N 6.3, 6.32. $C_7H_6O_2NSF_3$. Calculated %: N 6.22.

The acetyl derivative melted at 132-133°.

Found %: N 5.45, 5.5. $C_9H_6O_3NSF_3$. Calculated %: N 5.25.

p-Bromophenyltrifluoromethylsulfone.

3 g of p-aminophenyltrifluoromethylsulfone was diazotized and the amino group was replaced with bromine by the Sandmeyer reaction. The product was steam distilled. After crystallization from alcohol, the yield was 1.9 g (50%). The m.p. was 64-65°.

Found %: S 10.99, 10.75. $C_7H_4O_2SBrF_3$. Calculated %: S 11.07.

p-Iodophenyltrifluoromethylsulfone.

3 g of p-aminophenyltrifluoromethylsulfone was diazotized, and the amino group replaced with iodine, by the Sandmeyer reaction. After steam distillation, the product was crystallized from aqueous alcohol. The m.p. was 78-79°. The yield was 3 g (67%).

Found %: I 37.54, 37.88. $C_7H_4O_2SIF_3$. Calculated %: I 37.80.

p-Hydroxyphenyltrifluoromethylsulfone.

2 g. of p-aminophenyltrifluoromethylsulfone was stirred with a solution of sulfuric acid (1.5 ml of H_2SO_4 in 10 ml of water) and diazotized with sodium nitrite (0.8 g of $NaNO_2$ in 4 ml of water). Upon completion of the addition of the sodium nitrite, the mixture was stirred for 30 minutes at room temperature, and the solution was then heated until the diazonium salt was completely decomposed. After cooling, a brown precipitate settled out, which was filtered and crystallized from water. The m.p. was 119-120°. The yield was 1.16 g (58%).

Found %: S 14.23, 14.36. $C_7H_5O_3SF_3$. Calculated %: S 14.11.

The dibromide;

Prepared by adding bromine to an aqueous solution of p-hydroxyphenyltrifluoromethylsulfone. After crystallization from aqueous alcohol, the m.p. was 150°.

Found %: S 8.03, 7.95. $C_7H_3O_3SBr_2F_3$. Calculated %: S 8.3.

p-Cyanophenyltrifluoromethylsulfone.

10 g of p-aminophenyltrifluoromethylsulfone was diazotized and the amino group was replaced with the nitrile group by the Sandmeyer reaction. After complete decomposition of the cyanide complex of the diazonium salt, the

product was steam distilled and filtered. The yield was 5.2 g (50%). After crystallization from aqueous alcohol, the m.p. was 89-90°.

Found %: N 6.07, 6.13. $C_6H_4O_2NSF_3$. Calculated %: N 5.96.

p-Carboxyphenyltrifluoromethylsulfone.

2.4 g of p-cyanophenyltrifluoromethylsulfone was heated in a sealed tube with 6 ml of concentrated hydrochloric acid for 6 hours at 120-130°. After opening the tube, the acid was filtered, washed with water and crystallized from aqueous alcohol. The m.p. was 239-240°. The yield was 2.3 g (88%).

Found %: S 12.50, 12.74. $C_6H_4O_3SF_3$. Calculated %: S 12.59.

The acid chloride of the acid;

Prepared by boiling 2.3 g of the acid with 12 ml of thionyl chloride for 4 hours on a water bath. The excess thionyl chloride was distilled off and the product vacuum distilled. The b.p. was 149-150° at 20 mm, and the m.p. was 29-30°. The yield was 2 g (83%).

The ethyl ester.

Prepared by boiling the acid chloride of the acid with anhydrous ethyl alcohol. The b.p. was 148-149° at 10 mm, m.p. 47-48°.

The amide of the acid.

Prepared by two methods: 1) from the acid chloride and aqueous ammonia; m.p. 196-197° (from aqueous alcohol); 2) by saponifying the nitrile with aqueous-alcoholic alkali in the presence of hydrogen peroxide by Radziszewski's method [12]; m.p. 196-197°.

Found %: N 5.67, 5.78. $C_6H_5O_2NSF_3$. Calculated %: N 5.53.

2-Amino-6-trifluoromethylbenzthiazolylsulfone.

1.7 g of ammonium thiocyanate was added to a suspension of 2 g of p-aminophenyltrifluoromethylsulfone in 14 ml of glacial acetic acid, and while the mixture was being cooled and stirred, 1.7 g of bromine in 4 ml of glacial acetic acid was added. Upon completion of the addition of bromine, the mixture was stirred for 1 hour and left overnight. Water (60 ml) was then added and the mixture was heated to boiling, cooled and filtered. The free amine was isolated from the filtrate with soda. The product crystallized from aqueous alcohol. The yield was 1.2 g (50%). The m.p. was 220-221°.

Found %: N 9.79, 9.83. $C_6H_5O_2N_2S_2F_3$. Calculated %: N 9.93.

SUMMARY

30 compounds containing the SCF_3 and SO_2CF_3 groups as substituents in the benzene nucleus, were synthesized and their properties described.

LITERATURE CITED

- [1] French Patent 820796; Chem. Zentr. I, 1876 (1938); Amer. Pat. 503920; Chem. Zentr. II, 946 (1938); Scherer, Ang. Chem., 42, 457 (1939).
- [2] L. M. Yagupolsky and A. I. Kiprianov, J. Gen. Chem., 22, 2216 (1952); French Patent 828572; Chem. Zentr., II, 2503 (1938).
- [3] N. V. Smirnova, J. Gen. Chem., 17, 283 (1947); R. Cutler, R. Stenger, C. Suter, J. Am. Chem. Soc., 74, 5475 (1952); F. Johnson, C. Hamilton, J. Am. Chem. Soc., 71, 74 (1949).
- [4] Th. van Hove, Bull. Acad. roy. Belg., [5] 12, 929 (1927); Chem. Zentr. I, 1821 (1927).
- [5] K. Brand, K. Kranz, J. pr. Chem., [2] 115, 161 (1927); Chem. Zentr. I, 2727, (1927).
- [6] Th. Zincke, P. Jörg, Ber., 43, 3443 (1910).
- [7] Th. Zincke, C. Ebel, Ber., 47, 1105 (1914).
- [8] K. Kindler, Ann., 452, 90 (1927); Chem. Zentr. I, 2299 (1927).
- [9] R. Jones, J. Am. Chem. Soc., 69, 2346 (1947).
- [10] P. Pfeiffer, H. Iäger, Ber., 75, 1885 (1942).

[11] H. Holt, E. Reid, J. Am. Chem. Soc., 46, 2331 (1924).

[12] Br. Radziszewski, Ber., 18, 355 (1885).

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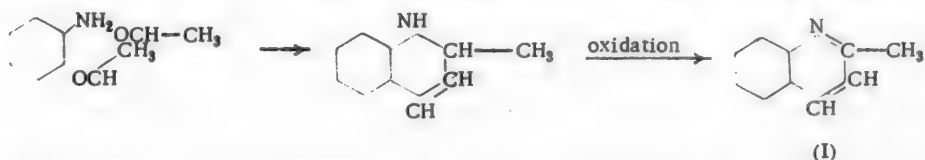
* See Consultants Bureau Translation, p. 2273.



PREPARATION OF QUINALDINE DERIVATIVES FROM AROMATIC AMINES AND VINYL ETHERS

B. A. Porai-Koshits, L. S. Efros, V. N. Vertkina and V. V. Lutsenko

Quinaldine is a valuable intermediate product which has found application in the synthesis of strong acidic and cyanine dyes. The reciprocal reaction of acetaldehyde with aniline is used at the present time to prepare it; in this reaction, quinaldine (I) is formed either directly [1] or via a stage of formation of a product of obscure structure (the so-called Schulz base [2]), which is fused by Lyashenko's method [3] with zinc chloride. The reaction in which quinaldine is formed by this method can be represented by the following scheme:



Nitrobenzene or its sulfonic acid [4] is usually used as the oxidizing agent which is necessary for the reaction. The yield of quinaldine by this method, even in the better modification of Lyashenko [3], does not exceed 50%.

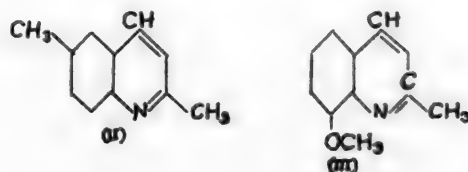
Since work with acetaldehyde involves a number of difficulties, while the vinyl ethers are at the present time in a number of cases more accessible than acetaldehyde, we determined to try to use these ethers for the synthesis of quinaldine and its derivatives. This work also proved to be interesting because up to the present time no one has studied the reaction of the vinyl ethers and primary aromatic amines, and, naturally, this question was not treated in Shostakovsky's monograph [5].

The very first experiments which we carried out involving the condensation of vinylbutyl ether with aniline in the presence of mineral acid, showed that this reaction proceeds very readily. The product obtained, after careful rectification, was identified in the form of the picrate with the picrate of known quinaldine. We then undertook to delineate the conditions for preparing quinaldine by this method, and found that there is a definite optimum acidity of the medium in which the reaction is carried out. This apparently indicates that here, just as in certain other reactions which are catalyzed by hydrogen ions [6], their role is dual: they activate the vinylbutyl ether and render the aniline passive, forming the unreactive phenylammonium ion with it.

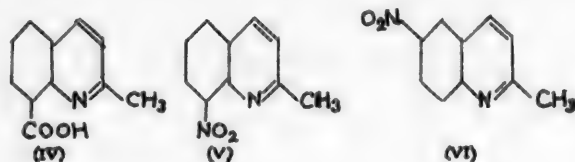
The yield of quinaldine, obtained by the optimal modification, amounts to 47-52%, i.e., does not exceed the yield of product by Lyashenko's method. However the simplicity and convenience of bringing about the reaction argues in favor of the practical value of preparing quinaldine from vinylbutyl ether.

We then attempted to use this reaction for the synthesis of quinaldine derivatives, using for this aniline which contained various substituents.

6-Methylquinaldine (II) was thereby obtained from *p*-toluidine; 8-methoxyquinaldine (III) from *o*-anisidine, while neither from *p*-aminophenol nor from *m*-phenylenediamine were quinaldine derivatives obtained; — only resinous products were formed.



In exactly the same way, the quinaldine derivatives (IV), (V) and (VI) were obtained from anthranilic acid and from *o*- and *p*-nitroaniline, while both *m*-nitroaniline and 2,4-dinitroaniline proved to be incapable of entering into the condensation:



Thus, the reaction of aromatic amines with vinyl ethers appears to be a general method for preparing quinaldine derivatives. The success of the reaction, however, depends on the character of the substituents which are found in the nucleus. In the case of the strongly activated molecules of a reactive amine (aminophenol, *m*-phenylenediamine), as well as in the case of deactivation, particularly of the *o*-position to the amino group (*m*-nitroaniline), quinaldine derivatives are not obtained.

The present work fulfills a project of A. E. Porai-Koshits.

EXPERIMENTAL

Preparation of quinaldine (optimal modification of the method). 25 g (0.25 mole) of vinylbutyl ether was added in the form of drops to a mixture of 12 g of aniline (0.13 mole), 5 g of nitrobenzene (0.04 mole) and 39 g concentrated HCl (0.4 mole) while the mixture was being stirred and heated on a boiling water bath. Upon completion of the addition of the ether, the mixture was heated for 30 minutes more and then the excess nitrobenzene was steam distilled off. The solution obtained was neutralized with 10% soda solution and the oil which was formed was extracted with 100 ml of ether. To separate the aniline [7] the ethereal solution was dried over roasted sodium sulfate, 9 g of phthalic anhydride was added, and the mixture was stirred for 1 hour. The mass was treated with 10% soda solution until the reaction of the aqueous layer was alkaline to brilliant yellow paper. The ethereal layer was separated, washed with water and dried with roasted sulfate, and the ether was distilled off at atmospheric pressure. The quinaldine which was left was distilled at 5 mm residual pressure, and the fraction which boiled at 99-101° was collected.

The yield of quinaldine was 8.2-9.3 g (44-50%). The product did not contain aniline (test with calcium hypochlorite). The melting point of the picrate was 193-194°.

Found: M 143.7 (potentiometric titration), 142 (cryometry in benzene), C₂₀H₉N. Calculated: M 143

6-Methylquinaldine. 6-Methylquinaldine was prepared in exactly the same way as quinaldine. After carrying out the reaction between 5.5 g of *p*-toluidine and 10.5 g of vinylbutyl ether in 16.5 ml of concentrated HCl, the reaction mass was neutralized with soda and the oil which was evolved was extracted with ether. The ethereal solution was treated with phthalic anhydride to separate the *p*-toluidine which had not reacted, and was distilled.

The oil which was obtained partially congealed on cooling; the product was separated and crystallized from ether. 6-Methylquinaldine with a m.p. of 57-59° was obtained. Its picrate had a m.p. of 178°. The literature data [8] are, respectively, 59-60° and 178°.

8-Methoxyquinaldine. 7.5 g of vinylbutyl ether was added in the form of drops to a mixture of 5.5 g of *o*-anisidine and 12 ml of concentrated HCl which was being heated on a water bath and being stirred. The reaction mass was kept under these conditions for 1 hour and then diluted with water and neutralized with 10% soda solution. The thick oil which precipitated was extracted with benzene; after a portion of the latter was distilled off, the colorless 8-methoxyquinaldine crystallized from the remaining solution on cooling; it melted at 123° [9] after one crystallization from benzene. The yield was 1.8 g (25%).

Quinaldine-8-carboxylic acid. 15 g of vinylbutyl ether was added in the form of drops to a mixture of 10.5 g of anthranilic acid and 24 ml of concentrated HCl while the mixture was being heated on a water bath and being stirred. The mass was kept under these conditions for 1 hour and then concentrated to dryness. The resinous residue was treated with a mixture of equal parts of alcohol and ether, after which the precipitate was dissolved in a small quantity of water. The aqueous solution was carefully neutralized with ammonia to a very weakly alkaline reaction with brilliant yellow paper as the indicator. The acid was isolated in the form of colorless needles with a m.p. of

147°, in a quantity of 3.4 g (24%). After crystallization from water, the m.p. was 154°.

6-Nitroquinaldine. 12 g of p-nitroaniline, 24 ml of concentrated HCl and 15 g of vinylbutyl ether were the starting materials for the synthesis. After neutralizing the reaction mass with soda, a yellow product was isolated which was twice reprecipitated with soda from a solution in dilute hydrochloric acid and crystallized from aqueous alcohol for purification. The yield of product with a m.p. of 165° was 7.4 g (45%).

8-Nitroquinaldine. The starting materials were 6 g of o-nitroaniline, 12 ml of concentrated HCl and 7.5 g of vinylbutyl ether. The reaction mass was diluted with water, filtered from resin and neutralized with a 10% solution of soda. A black resinous product precipitated which slowly solidified. It was separated, dissolved in concentrated HCl, the solution filtered free of contamination and neutralized with ammonia; a yellow precipitate thereupon settled out which was crystallized from dilute alcohol. The long yellow needles of 8-nitroquinaldine melted at 139°. The yield was 3.6 g (44%).

SUMMARY

The reciprocal reaction of primary aromatic amines with vinyl ethers leads to the formation of quinaldine derivatives.

LITERATURE CITED

- [1] Miller, Döbner. Ber., 16, 2464 (1883); Fndl., I, 186.
- [2] Schulz, Ber., 16, 2601 (1883).
- [3] V. D. Lyashenko, Author's Certificate No. 26668.
- [4] German Patent 567273.
- [5] M. F. Shostakovsky. Vinyl Ethers. Moscow, Acad. Sci. USSR Press (1952).
- [6] B. A. Porai-Koshits, O. F. Ginzburg and L. S. Efros, J. Gen. Chem., 17, 1768 (1947).
- [7] B. A. Porai-Koshits. Author's Certificate No. 47297.
- [8] Döbner, Ber., 33, 679 (1900).
- [9] Miller, Döbner, Ber., 17, 1699 (1884).

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1. The first part of the paper is devoted to a general discussion of the problem of the existence of a solution of the system of equations

$$\frac{dx}{dt} = A(x)u, \quad \frac{dy}{dt} = B(y)v, \quad (1)$$

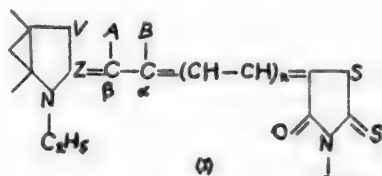
where $A(x)$ and $B(y)$ are matrices depending on x and y respectively, and u and v are vectors.

MEROCYANINE DYES DERIVED FROM RHODANINE

VI. DIMETHINEMEROCYANINES CONTAINING THE ALKYL OR PHENYL GROUP IN THE POLYMETHINE CHAIN

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In preceding works [1,2], devoted to the investigation of merocyanine derivatives of rhodanine (I; A and B = H; n = 0, 1 or 2), we studied the influence of the nature of the heterocyclic nitrogen-containing radicals and the long external polymethine chain on the properties of these dyes:

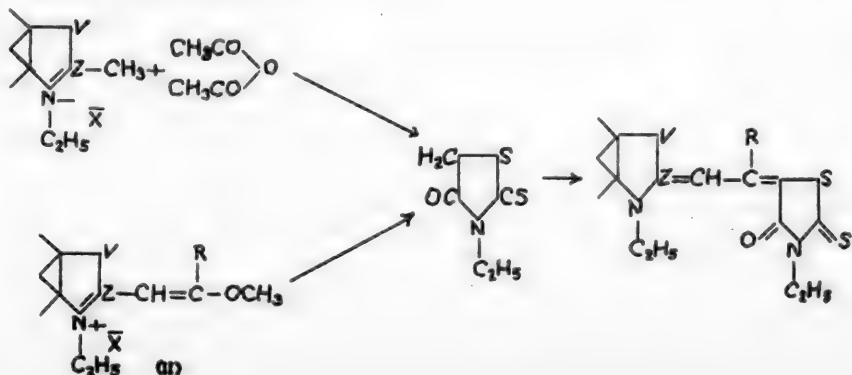


where V = O, S, Se, CH=CH, C(CH₃)₂, N-CH₃, etc.; Z = carbon or the =CH-C=C- group (in the latter case the V grouping is absent); n = 0, 1 or 2.

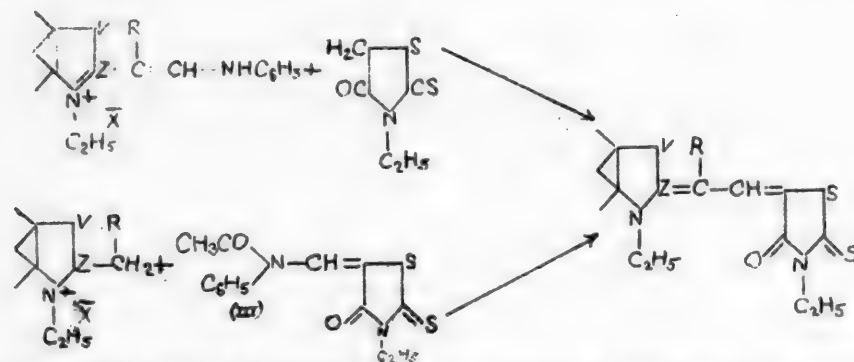
The entrance of substituent groups into the polymethine chain of the cyanine dyes exerts a considerable influence on their color [3-12], and, depending on the character and position of the substituents, and also on the nature of the heterocyclic nitrogen-containing residue, either a bathochromic or a hypsochromic displacement of the absorption maximum can be observed.

The question of the influence of substituents in the polymethine chains of the merocyanines on their color has still been investigated very little. A number of chain-substituted merocyanines have been presented in the patent literature which have been proposed as sensitizers for silver halide photographic emulsions [13-16]. The positions of the absorption and activation maxima have been presented for certain of these dyes. A few of the works of A. van Dormael with his coworkers have been devoted to the synthesis and investigation of dimethinemerocyanines which contain various complex substituents in the meso position [17, 18]. However, it is not possible on the basis of these data to draw definite conclusions concerning the influence of the presence of substituents in the polymethine chain on the color of the merocyanines. In this connection, we synthesized a number of α - and β -alkyl- and phenyl-substituted dimethylmerocyanine derivatives of 3-ethylrhodanine (I; n = 0), which differ in the nature of the heterocyclic nitrogen-containing radicals, and investigated their absorption spectra in alcoholic solutions.

Meso-methyl substituted merocyanines with benzthiazole, benzoxazole, thiazoline, 4-phenylthiazole and 6-dimethylaminobenzthiazole radicals (I; A = H; B = CH₃) were synthesized with satisfactory yields by heating the quaternary salts of the corresponding bases, containing the methyl group in the 2 position, with 3-ethylrhodanine and acetic anhydride in pyridine (cf. [13a]).



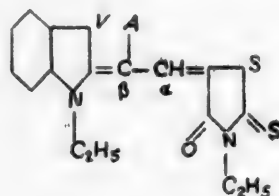
For the synthesis of meso-ethyl- and phenyl-substituted merocyanine derivatives of benzthiazole, and also of β -naphthothiazole and benzselenazole with a methyl group at the central carbon atom of the polymethine chain, the quaternary salts of 2- β -methoxy-[19;20] or methylmercaptoalkenyl derivatives [15 a] of the corresponding bases (II) were used which were condensed with 3-ethylrhodanine in propanol in the presence of triethylamine. It was also found that in the reaction of 3-ethylrhodanine with the quaternary salts of 2- β -anilinobutenylbenzoxazole and 2- β -anilinoisobutenylbenzthiazole, the corresponding α - and β -ethyl substituted merocyanines are formed. The most satisfactory yields in these cases were obtained by carrying out the reaction in a mixture of butanol and pyridine in the presence of triethylamine.



We succeeded in preparing β -substituted merocyanines with the benzthiazole and benzoxazole radicals by condensing the quaternary salts of 2-ethyl- and 2-benzyl-benzthiazole and also of 2-ethylbenzoxazole with 3-ethyl-5-aceanilinothiopyran (III) in a mixture of butanol and pyridine in the presence of triethylamine. More deeply colored salt-like dyes were formed as by-products in this reaction; they were separated by chromatographing them on aluminum oxide.

The absorption maxima and molar extinction coefficients (ϵ) of dimethylmerocyanines with the benzthiazole and benzoxazole radicals which contain substituents in the beta-position of the polymethine chain, are presented in table 1.

TABLE 1
General Formula:



A	V = S			V = O		
	$\lambda_{\max.}$ (m μ)	$\epsilon \cdot 10^{-4}$	Displacement in comparison with the unsubstituted dye (in m μ)	$\lambda_{\max.}$ (m μ)	$\epsilon \cdot 10^{-4}$	Displacement in comparison with the unsubstituted dye (in m μ)
H ..	524	11.31	—	492	8.05	—
CH ₃ ..	540	11.29	16	510	13.25	18
C ₂ H ₅ ..	540	8.35	16	—	—	—
C ₆ H ₅ ..	536	9.40	12	—	—	—

As is evident from Table 1, the entrance of alkyl groups, and also of the phenyl group into the beta position of these dyes causes a deepening of the color. The absorption coefficient remains unchanged under these conditions in the case of the thia-derivatives, or is somewhat lowered, while it is appreciably increased for dyes with the benzoxazole residue.

It can be assumed by analogy with the 8,10-substituted thiacyanines [6] that the bathochromic displacement of the absorption maximum observed in the β -substituted merocyanines is associated with disturbance of the plane structure of their molecules, due to the closeness of the substituting groups in the external chain to the heterocyclic radical. It is rather strange that the coefficient of absorption

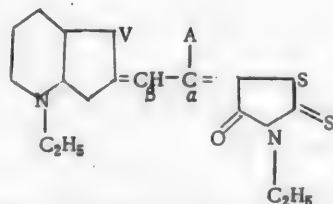
of the merocyanines investigated is not lowered relative to that of the unsubstituted dyes. However, a similar phenomenon was also observed in the case of 8,10-di- and trimethylenethiacyanines [7,9], the deep color of which, evidently, is associated with disturbance of the plane structure of their molecules. The absorption maxima of α -substituted merocyanines with the benzthiazole and benzoxazole radicals are given in Table 2.

As is evident from Table 2, entrance of substituents into the α -position of merocyanines with the benzthiazole radical causes a bathochromic displacement of the absorption maximum which reaches 18 m μ in the case of the phenyl group. The bathochromic influence of the alkyl groups is still more significant for dyes with the benzoxazole radical. It is well known that in the case of thiacyanines, a methyl group in the meso-position causes a hypsochromic displacement equal to 14 m μ [3-5], while for oxa- and thiazolinocyanines, on the other hand, the absorption maximum is displaced into the long-wave region under these conditions [3, 12].

From this point of view, it was of interest to investigate the α -methyl-substituted merocyanines with nitrogen-containing radicals of varying basicity. The absorption maxima of a number of α -methyl substituted merocyanines are set forth in Table 3, and are arranged in the order of increasing bathochromic influence of the methyl group. It is evident from the data of Table 3, that the entrance of a methyl group at the central carbon atom of the polymethine chain, in the case of the merocyanine with the 4-phenylthiazole radical, causes an insignificant hypsochromic displacement of the absorption maximum; as one proceeds to dyes with radicals which are less basic, this effect becomes bathochromic and increases all the more as the basicity of the nitrogenous heterocyclic radical decreases.

TABLE 2

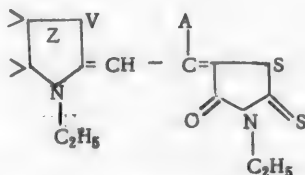
General Formula:



A	V = S		V = O	
	$\lambda_{\max.}$ (in μ)	Displacement in comparison with the unsubstituted dye (in μ)	$\lambda_{\max.}$ (in μ)	Displacement in comparison with the unsub- stituted dye (in μ)
H.	524	—	492	—
CH ₃	532	8	504	12
C ₂ H ₅	536	12	506	14
C ₆ H ₅	542	18	—	—

TABLE 3

General formula:



Heterocyclic nitrogenous rad- ical Z	$\lambda_{\max.}$ (in μ)		Displacement (in μ)
	A = H	A = CH ₃	
4-Phenylthiazole	538	536	-2
6-Dimethylamino- benzthiazole	553	556	+3
8-Naphthothiazole	542	548	+6
Benzselenazole	524	532	+8
Benthiazole	524	532	+8
Benzoxazole	492	512	+12
Thiazoline	482	495	+13

was triturated with 50 ml of ethyl alcohol and the precipitate was filtered off and washed with alcohol. The yield was 2.2 g (53.5%). The m.p. was 179-181°. The product was crystallized from ethyl alcohol (1. part per 12 ml) for purification. The weight was 1.7 g. It consisted of pinkish flakes with a m.p. of 183-184°.

Found %: N 6.77. C₁₉H₂₁ON₂I Calculated %: N 6.66.

The quaternary salts of the heterocyclic nitrogen-containing bases were synthesized by heating equimolecular quantities of the base and the ethyl ester of *p*-toluenesulfonic acid in a flask with an air condenser, equipped with a calcium chloride tube. The condition of the heating were as follows: for the ethyl-*p*-toluenesulfonates of 2-methylbenzthiazole (III), 2-methyl-6-dimethylaminobenzthiazole (IV) and 2-ethylbenzthiazole (V) — 4 hours at 140-145°, for the same esters of 2-methylbenzoxazole (VI) and 2-methyl-4-phenylthiazole (VII) — 5 hours at 140-145°, and for the ester of 2-methylthiazoline (VIII) — 1 hour at 120-125°. The ethyl-ethylsulfate of 2-benzylbenzthiazole (XV) was prepared analogously, by heating base with diethyl sulfate for 6 hours at 130°. The quaternary salts were

In the slightly basic merocyanines, the electron displacements from the nitrogen atom toward the carbonyl oxygen are evidently relatively small, as a consequence of which the electron density is irregularly distributed in their chromophore. The entrance of an electropositive methyl group at the central carbon atom of the polymethine chain of these dyes should lead to increasing of the electron displacement at the oxygen and, consequently to the equalization of the electron density in the chromophore, as a result of which deepening of the color can be expected.

When the basicity of the heterocyclic nitrogen-containing radical of the dimethinemerocyanine derivatives of rhodanine is increased, their polarity is considerably increased [1, 21-24]. In this case,

the entrance of a methyl group at the central carbon atom of the polymethine chain should still more increase the polarity of the dye, and can lead to diminishing the regularity of the distribution of the electron density in the chromophore, and, in connection with this, to an intensification of the color.

The experimental data obtained by us concerning the influence of the methyl group in the meso-position of the polymethine chain of merocyanines on their color are in complete agreement with the considerations indicated above.

EXPERIMENTAL

Iodoethylate of 2- β -anilinopropenylbenzoxazole.

A mixture of 2.9 g of the iodoethylate of 2-methylbenzoxazole and 3.1 g of ethylisothiopropionanilide was heated for 1 hour at 160° in a round-bottomed flask with an air condenser. The solid reaction mass

TABLE 4

Dye	Quantity (g)			Solvent	
	Of I or II	Of acetic anhydride	Of the quaternary salt	Formula	Quantity (in ml)
3-Ethyl-5-[3'-ethyl-4'-phenyl-thiazolinyli- den-2'-(α -methyl)- ethyliden]-thiazolidinthion -(2)- one-(4)	0.48 (I)	0.9	1.12 (VII)	C ₅ H ₅ N	3.5
3-Ethyl-5-[3'-ethyl-6'-dimethylam- inobenzthiazolinyli- den-2'-(α -methyl)- ethyliden]-thiazolidinthion -(2)-one- (4)	0.48 (I)	0.9	1.17 (IV)	C ₅ H ₅ N	3.5
3-Ethyl-5-[3'-ethyl-4',5'-benzobenzthi- azolinyli- den-2'-(α -methyl)-ethyliden]- thiazolidinthion -(2)-one-(4) [14a]	0.19 (I)	—	0.43 (XIII)	n-C ₄ H ₉ OH	2
3-Ethyl-5-[3'-ethylbenzselena- zolinyliden-2'-(α -methyl)-ethyliden]-thiazo- lidinthion -(2)-one-(4) [19]	0.19 (I)	—	0.41 (XIV)	n-C ₃ H ₇ OH	1.5
3-Ethyl-5-[3'-ethylbenzthiazolinyli- den-2'-(α -methyl)-ethyliden]-thiazol- idinthion -(2)-one-(4) [13a, 25]	3.2 (I)	6	6.98 (III)	C ₅ H ₅ N	24
3-Ethyl-5-[3'-ethylbenzoxazolinyli- den-2'-(α -methyl)-ethyliden]-thiazolidin- thion -(2)-one-(4)	3.2 (I)	6	6.66 (VI)	C ₅ H ₅ N	24
3-Ethyl-5-[3'-ethylthiazolidinyli- den-2'-(α -methyl)-ethyliden]-thiazolidin- thion -(2)-one-(4)	0.64 (I)	1.2	1.2 (VIII)	C ₅ H ₅ N	5
3-Ethyl-5-[3'-ethylbenzthiazolinyli- den-2'-(α -ethyl)-ethyliden]-thiazolidinthion - (2)-one-(4) [13d]	0.57 (I)	—	1.47 (XVI)	n-C ₃ H ₇ OH	4
3-Ethyl-5-[3'-ethylbenzoxazolinyli- den-2'-(α -ethyl)-ethyliden]-thiazolidinthion (2)-one-(4)	0.16 (I)	—	0.42 (X)	C ₅ H ₅ N n-C ₄ H ₉ OH	0.5 1
3-Ethyl-5-[3'-ethylbenzthiazolinyli- den-2'-(α -phenyl)-ethyliden]-thiazolidin- thion -(2)-one-(4) [15a]	0.2 (I)	—	0.48 (XII)	n-C ₃ H ₇ OH	1.5
3-Ethyl-5-[3'-ethylbenzthiazolinyli- den-2'-(β -methyl)-ethyliden]-thiazolidin- thion -(2)-one-(4)	0.36 (II)	—	0.52 (V)	C ₅ H ₅ N n-C ₄ H ₉ OH	0.5 1
3-Ethyl-5-[3'-ethylbenzoxazolinyli- den-2'-(β -methyl)-ethyliden]-thiazolidin- thion -(2)-one-(4)	0.61 (II)	—	0.6 (IX)	C ₅ H ₅ N n-C ₄ H ₉ OH	0.8 1.5
3-Ethyl-5-[3'-ethylbenzthiazolinyli- den-2'-(β -ethyl)-ethyliden]-thiazolidinthion - (2)-one-(4)	0.16 (I)	—	0.41 (XI)	C ₅ H ₅ N n-C ₄ H ₉ OH	0.5 1
3-Ethyl-5-[3'-ethylbenzthiazolinyli- den-2'-(β -phenyl)-ethyliden]-thiazolidin- thion -(2)-one-(4)*	0.9 (II)	—	1.13 (XV)	C ₅ H ₅ N n-C ₄ H ₉ OH	1.2 2.5

* The dye was purified by chromatographing it on aluminum oxide

	Triethylamine (in g)	Duration of boiling (in minutes)	Yield (in%)	Quantity of ethyl alcohol for cry- stallization (ml/ g)	Superficial form	M.p.	Analysis		
							Found content of N (in %)	Calculated	
								Empirical formula	N (in %)
—	90	30.9	500	Fine dark red needles	230-231°	7.20	C ₁₉ H ₂₀ ON ₂ S ₃	7.21	
—	90	24.6	100	Shiny green prisms	249-250	••	C ₁₉ H ₂₂ ON ₂ S ₃	••	
0.1	30	19.3	1650	Fine, dark red needles	243	7.00	C ₂₁ H ₂₀ ON ₂ S ₃	6.78	
0.1	30	34.2	500	Shiny, dark red prisms	202-203	6.60	C ₁₇ H ₁₈ ON ₂ S ₂ S	6.84	
—	90	15.4	1400	Shiny, violet prisms	217-218	7.57	C ₁₇ H ₁₈ ON ₂ S ₃	7.72	
—	90	28	1100	Brown needles with a green luster	222-224	7.95	C ₁₇ H ₁₈ O ₂ N ₂ S ₂	8.11	
—	120	27	230	Red prisms	187-188	9.01	C ₁₃ H ₁₈ ON ₂ S ₃	8.90	
0.15	10	15	100	Violet prisms	162-164	7.64	C ₁₈ H ₂₀ ON ₂ S ₃	7.44	
0.1	45	27.7	120	Fine red needles	165-167	7.71	C ₁₈ H ₂₀ O ₂ N ₂ S ₂	7.77	
0.12	10	25.6	70	Violet prisms	245-247	6.75	C ₂₂ H ₂₀ ON ₂ S ₃	6.59	
0.1	60	58	400	Violet flakes	205-207	7.70	C ₁₇ H ₁₈ ON ₂ S ₃	7.72	
0.22	120	34.6	250	Red needles	209-210	8.03	C ₁₇ H ₁₈ O ₂ N ₂ S ₂	8.08	
0.1	45	58	••• 37	Shiny green flakes	177-178	7.49	C ₂₈ H ₂₀ ON ₂ S ₃	7.43	
0.3	150	9.4	220	Dark red prisms	210-212	6.37	C ₂₂ H ₂₀ ON ₂ S ₃	6.59	

•• Found % S 23.73%, calculated % S 23.71%.

••• Toluene

used to prepare the dyes without purification. The ethylmethylsulfates of 2- β -methoxy and β -methylmercapto-alkenyl derivatives of the heterocyclic nitrogenous bases were synthesized analogously, by heating the corresponding acyl- and thioacylmethylene compounds with dimethylsulfate. The conditions of heating for the ethylmethylsulfates of 2- β -methoxypropenyl- β -naphthothiazole (XIII) (1 hour at 140°), 2- β -methoxypropenylbenzelenazole, (XIV) (30 minutes at 120°), and for the ethylmethylsulfates of 2- β -methylmercaptobutenylbenzthiazole (XVI) and 2- β -methylmercaptostyrylbenzthiazole (XII) (10 minutes at 120°) were as indicated.

Synthesis of the merocyanines . The conditions for preparing the merocyanines, the yields, the melting points of the dyes and the analytical results are set forth in Table 4. The following symbols have been adopted for the initial products in this table: 3-ethylrhodanine - I, 3-ethyl-5-acetanilinomethylenrhodanine - II, iodoethylate of 2-ethylbenzoxazole - IX, iodoethylate of 2- β -anilinopropenyl-benzoxazole - X, ethylperchlorate of 2- β -anilinoisobutenylbenzthiazole - XI. The conventional symbols for the quaternary salts of the heterocyclic bases and their derivatives are set forth above in the description of the synthesis (III - VIII and XII - XVI).

In all cases, the dyes which were formed on cooling were filtered off, washed with water and ethyl alcohol, and recrystallized to constant melting point. In certain cases, preliminary chromatography on aluminum oxide in benzene solution was utilized.

SUMMARY

1. A number of dimethinemerocyanine derivatives of 3-ethylrhodanine with various heterocyclic nitrogenous radicals containing the alkyl or phenyl group in the alpha or beta positions of the polymethine chain were synthesized.
2. It was made clear that the introduction of an alkyl or phenyl group into the alpha or beta positions of the polymethine chain of the dimethinemerocyanines with the benzthiazole and benzoxazole radicals causes a bathochromic displacement of the absorption maximum.
3. It was shown that the bathochromic displacement of the absorption maximum caused by the introduction of the methyl group into the alpha position of the external polymethine chain of the merocyanines which were investigated, diminishes with increasing basicity of the nitrogenous heterocyclic radical, and in the case of the dye with a 4-phenylthiazole radical, becomes hypsochromic.

LITERATURE CITED

- [1] M. V. Deichmeister, Z. P. Sytnik and E. B. Lifshits, J. Gen. Chem., 22, 166 (1952). *
 - [2] M. V. Deichmeister, I. I. Levkoev, and E. B. Lifshits, J. Gen. Chem., 23, 1529 (1953). * *
 - [3] L. G. S. Brooker, F. L. White, J. Am. Chem. Soc., 57, 547, 2480 (1935); L. G. S. Brooker, J. Am. Chem. Soc., 58, 662 (1936).
 - [4] A. I. Kiprianov, N. E. Grigoryeva, Trans. Inst. Chem. Khar'kov Univ., 3, 53 (1937).
 - [5] A. I. Kiprianov, Z. P. Sytnik, E. D. Sych, J. Gen. Chem., 6, 43 (1936).
 - [6] A. I. Kiprianov, I. K. Ushenko, J. Gen. Chem., 20, 134, 514 (1950). * * *
 - [7] A. I. Kiprianov, I. K. Ushenko, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 5, 492 (1950).
 - [8] I. K. Ushenko, Ukr. Chem. J., 14, 50 (1948); 16, 450 (1950).
 - [9] A. I. Kiprianov, Anniversary Collection Acad. Sci. Ukr. SSR 40 (1947).
 - [10] A. I. Kiprianov, Yu. S. Rozum, Collection Sci. Work. Inst. Org. Chem. Acad. Sci. Ukr. USSR, No. 13, 29 (1947).
 - [11] N. N. Svesnikov, I. I. Levkoev, B. S. Portnaya, E. B. Lifshits, Proc. Acad. Sci. USSR, 84, 733 (1952).
 - [12] H. C. Barany, M. Planka, J. Chem. Soc., 1953, 2217.
 - [13] Ilford Ltd., Brit. Pat.: a) 485110, b) 487051, c) 624027, d) 519895.
 - [14] Kodak Ltd., Brit. Pat.: a) 466097, b) 606141.
 - [15] I. G. Farben-ind. A. G., French Patent: a) 881041, b) 879306.
 - [16] Eastman Kodak Co., U. S. Pat. 2493747, 2493748, 2494031, 2478366, 2519001.
 - [17] A. van Dormael, Ind. Chim. Belg., 17, 665 (1952); A. van Dormael, J. Nys, Bull. Soc. Chim. Belg., 62, 199 (1953).
- * See Consultants Bureau Translation, p. 209. ** See Consultants Bureau Translation, p. 1601. *** See Consultants Bureau Translation, p. 1601.

- [18] P. Bruylants, A. van Dormael, *Rec. trav. chim.*, 69, 321 (1950).
- [19] N. N. Sveshnikov, I. I. Levkoev, M. V. Deichmeister, A. F. Vompe, Author's Certificate 92159.
- [20] N. N. Sveshnikov, I. I. Levkoev, A. F. Vompe, B. S. Portnaya, *Proc. Acad. Sci. USSR*, 88, 281 (1953).
- [21] L. G. S. Brooker, *Frontiers in Chemistry*, III, 63 (1945).
- [22] A. I. Kiprianov, E. S. Timoshenko, *J. Gen. Chem.*, 17, 1468 (1947).
- [23] I. I. Levkoev, N. N. Sveshnikov, E. B. Lifshits, *Proc. Acad. Sci. USSR*, 74, 275 (1950).
- [24] L. G. S. Brooker, G. H. Keyes, R. H. Sprague, R. H. van Dyke, E. van Lare, G. van Zandt, F. L. White, H. W. Cressman, S. G. Dent, *J. Am. Chem. Soc.*, 73, 5332 (1951).
- [25] L. G. S. Brooker, R. H. Sprague, R. H. van Dyke, E. van Lare, G. van Zandt, F. L. White, *J. Am. Chem. Soc.*, 73, 5326 (1951).

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PREPARATION OF ALIPHATIC-AROMATIC N-BIS-(CHLOROETHYL)-AMINES

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Aliphatic-aromatic N-bis-(chloroethyl)-amines, $[\text{Ar}(\text{CH}_2)_n\text{N}(\text{CH}_2\text{CH}_2\text{Cl})_2]$ have been comparatively little studied, although they are of undoubted interest for biological research. In the present work, we prepared new compounds of this type, specifically, benzyl-N-bis-(chloroethyl)-amines with alkoxy groups in the aromatic nucleus; in addition, certain other analogous compounds were also synthesized. In the synthesis of benzyl-N-bis-(chloroethyl)-amines, the most convenient method proved to be that [1] in which the starting materials are aromatic chloromethylated compounds of the (ArCH_2Cl) type. The N-bis-(hydroxyethyl)-benzylamines, $[\text{ArCH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2]$, are formed by the action on them of diethanolamine, and the hydroxy groups are replaced by halogen by any method. The success of the synthesis depends, in large measure, on the availability of the initial chloromethylated compound and on its properties.

Almost all of the initial chloromethylated alkoxycompounds were obtained by us by the action of paraform and hydrogen chloride in an anhydrous benzene medium on phenol ethers, and only 4-methoxy-3-nitrobenzylchloride was prepared by the action on o-nitroanisole of formalin and hydrogen chloride in the presence of zinc chloride [2].

In addition, we used other methods, for the most part ones which have already been described in the literature for example: β -chloromethylnaphthalene was prepared by chlorinating β -methylnaphthalene [3] p-cyanobenzylbromide, by the bromination of p-tolunitrile [4], while the o- and m-methoxybenzylchlorides were prepared from the corresponding methoxybenzyl alcohols by replacing the hydroxy group with chlorine [5].

We utilized new data in working out the methods for preparing certain of the starting materials, to wit, m-methoxybenzyl alcohol and m-methoxybenzoic acid. We prepared m-methoxybenzoic acid by oxidizing m-methoxyacetophenone with sodium hypochlorite; there is no reference to such a method of preparing it in the literature. The conversion of m-methoxybenzoic acid into m-methoxybenzyl alcohol was accomplished previously [6] by electrolytic reduction; we reduced this acid with the aid of lithium aluminum hydride; in addition, we prepared the amide of the acid and reduced it to the methoxybenzyl alcohol by means of a sodium amalgam. Both this and the other method gave completely satisfactory results, but the first of them (LiAlH_4) is more convenient for experimental work.

In the majority of cases, the condensation of all of the chloromethylated compounds obtained was carried out without solvent, and the latter was required only in the condensation of m-methoxybenzylchloride and p-methoxy-m-nitrobenzylchloride. Either benzene or chloroform was used as solvent. The substituted benzyl-bis-(hydroxyethyl)-amines formed as a result of the condensation were not isolated in the pure form, but after the condensation had been carried out, they were at once subjected to the action of thionyl chloride. The benzyl-N-bis-(chloroethyl)-amines thus obtained were isolated either in the form of the bases, or in the form of the hydrochlorides (Table 1).

EXPERIMENTAL

Chloromethylation of the phenol ethers. 1.4 Mole of paraform (well ground and screened through a fine sieve) was required per mole of phenol ether, and anhydrous benzene was required in a 4-fold quantity in relation to the quantity of phenol ether; a stream of hydrogen chloride was passed into the mixture obtained for 4.5 hours at a temperature of 0° . The small colorless precipitate which was left was filtered off, and the benzene solution was treated in the usual way. After distilling off the benzene, the residue was vacuum distilled. The chloromethylated compounds presented in Table 2, were obtained in this manner.

m-Methoxy benzoic acid 10 g of m-methoxyacetophenone was gradually added to sodium hypochlorite, prepared by saturating a mixture of 30 g of sodium hydroxide, 40 ml of water and 40 g of ice with chlorine until the weight increase amounted to 21.5 g. As the reaction proceeded, evolution of heat and strong foaming was observed; by external cooling with ice, the temperature was prevented from rising above 80° due to the heat evolution. After adding the m-methoxyacetophenone, the reaction mixture was stirred for 1.5 hours more, and then the solution was filtered off and sodium bisulfite was added to the filtrate in the required quantity. The m-meth-

TABLE 1

Compounds of the structure $\text{ArCH}_2\text{N}(\text{CH}_2\text{CH}_2\text{Cl})_2$

Ar	B.p. of the base	M.p. of the hydrochloride	Formula of the hydrochloride	Solvent	Carbon (in %)		Hydrogen (in %)		Nitrogen (in %)		Chlorine (in %)	
					Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
$\text{p-CH}_3\text{OC}_6\text{H}_4\text{--}$	150–160° at 5 mm	105–107°	$\text{C}_{13}\text{H}_{18}\text{ONCl}_3$	Benzene	48.24	48.28	6.03	6.23	4.69	4.55	35.67	35.92
$\text{o-CH}_3\text{OC}_6\text{H}_4\text{--}$	154–156° at 3 mm	124–125.5	$\text{C}_{13}\text{H}_{18}\text{ONCl}_3$	Benzene-chloroform mixture	48.24	48.22	6.03	6.26	4.69	4.55	35.67	36.05
$\text{m-CH}_3\text{OC}_6\text{H}_4\text{--}$	159–163° at 2–3 mm	101–103	$\text{C}_{13}\text{H}_{18}\text{ONCl}_3$	Toluene	48.24	48.58	6.03	6.16	4.69	4.75	35.67	35.62
$\text{p-C}_2\text{H}_5\text{OC}_6\text{H}_4\text{--}$	165–167° at 2–4 mm	120–121.5	$\text{C}_{15}\text{H}_{20}\text{ONCl}_3$	Benzene	50.43	50.24	6.81	6.44	4.51	4.53	34.30	34.07
$\text{p-C}_3\text{H}_7\text{OC}_6\text{H}_4\text{--}$	165–170° at 2–3 mm	124.5–126.5	$\text{C}_{16}\text{H}_{22}\text{ONCl}_3$	Benzene	51.46	51.96	6.74	6.58	4.28	4.37	32.62	32.08
$\text{p-iso-C}_3\text{H}_7\text{OC}_6\text{H}_4\text{--}$	167–170° at 3–4 mm	148.5–150.5	$\text{C}_{16}\text{H}_{22}\text{ONCl}_3$	Benzene	51.46	51.58	6.74	6.52	4.28	4.45	32.62	32.59
$\text{p-C}_4\text{H}_9\text{OC}_6\text{H}_4\text{--}$	178–184° at 2–4 mm	129–130	$\text{C}_{17}\text{H}_{24}\text{ONCl}_3$	Benzene	52.87	53.02	7.04	7.02	4.11	4.33	31.25	31.31
$3,4\text{-(CH}_3\text{O)}_2\text{C}_6\text{H}_3\text{--}$	160–170° at 2–3 mm	175–176	$\text{C}_{15}\text{H}_{20}\text{O}_2\text{NCl}_3$	Benzene-alcohol mixture	47.48	47.57	6.08	5.93	4.26	4.57	32.42	32.33
$4\text{-CH}_3\text{O-3-NO}_2\text{C}_6\text{H}_3\text{--}$	—	130–132	$\text{C}_{12}\text{H}_{17}\text{O}_3\text{N}_2\text{Cl}_3$	Methyl alcohol	41.92	42.24	4.94	5.28	8.15	8.50	—	—
$\text{p-CNOC}_6\text{H}_4\text{--}$	—	125.5–127.5	$\text{C}_{13}\text{H}_{15}\text{N}_3\text{Cl}_3$	Benzene-alcohol mixture	49.06	49.24	5.11	5.06	9.54	9.44	36.28	35.81
$\beta\text{-C}_{10}\text{H}_7\text{--}$	—	161–163	$\text{C}_{15}\text{H}_{19}\text{NCl}_3$	Ethyl acetate-alcohol mixture	56.50	56.69	5.65	5.78	4.39	4.27	33.44	33.12

oxybenzoic acid was isolated by acidifying the solution with hydrochloric acid; after recrystallization from water, the acid melted at 105–106°; the yield was 7 g.

The amide of *m*-methoxybenzoic acid was prepared from the methyl ester of the acid, prepared by esterification in the presence of sulfuric acid. A mixture of 10 g of the methyl ester of *m*-methoxybenzoic acid and 25 ml of aqueous ammonia was placed in a thick-walled vessel and saturated, while being cooled, with gaseous ammonia, after which the vessel was tightly covered and the mixture was shaken at room temperature for 30 hours. The amide of the acid which precipitated melted at 132–134° after recrystallization from alcohol; it was insoluble in water, difficultly soluble in benzene and soluble in alcohols.

6.885 mg substance; 0.559 ml N_2 (24°, 727 mm). Found %: N 8.92. $\text{C}_9\text{H}_9\text{O}_2\text{N}$. Calculated %: N 9.27.

***m*-Methoxybenzyl alcohol.** a) 5 g of *m*-methoxybenzoic acid, dissolved in a mixture of 140 ml of dry ether and 100 ml of benzene, was gradually added to 1.88 g lithium aluminum hydride in 40 ml of dry ether; a vigorous evolution of heat was thereupon observed; after the addition of the *m*-methoxybenzoic acid, the stirring and heating were continued for 1 hour and the mixture was then cooled and initially 11–12 ml of water and then a solution of 7.8 ml of sulfuric acid in 156 ml of water was added; the ether-benzene layer was separated, washed with water and dried. After distilling off the solvents, the residue was vacuum distilled; the b.p. was 130–135° at 11–12 mm, and the yield, 3 g.

b) 200 g of 5% sodium amalgam was added in small portions to a mixture of 4 g of the amide of *m*-methoxybenzoic acid, 30 ml of alcohol and 30 ml of water, with the acidity of the solution being maintained by the addition initially of acetic acid and then of 50% sulfuric acid. Upon completion of the reaction, the mercury was separated, the aqueous layer was neutralized with 20% NaOH solution and the alcohol was driven off in a vacuum, after which the solution was extracted with ether. After distilling off the ether, the residue was vacuum distilled, 1.8 g of the methoxybenzyl alcohol with a b.p. of 130° at 20–25 mm was obtained.

***m*-Methoxybenzyl chloride** was prepared by the action of phosphorus trichloride on *m*-methoxybenzyl alcohol in a chloroform solution; the b.p. was 106–108° at 12–14 mm.

Preparation of substituted benzyl-bis-(chloroethyl)-amines. 0.98 mole of diethanolamine which was heated to 65° was placed in a flask equipped with a stirrer, a reflux condenser, a thermometer and a dropping funnel. The corresponding chloromethylated compounds (ArCH_2Cl) were added

in the form of drops at this temperature, and while the mixture was being stirred at such a rate that the temperature within the reaction mixture did not rise above 75-80°; the reaction mass was then heated for 4-5 hours more at a temperature of 95-98°, after which it was cooled to 65° and a benzene solution of thionyl chloride (6 moles) was gradually added, and the solution again heated for 3 hours (temperature in the flask around 80°); the benzene and excess thionyl chloride were then distilled off in a vacuum. The oily substance left was dissolved in water, separated

TABLE 2

Formula	B. p.	Yield (in %)
p-CH ₃ OC ₆ H ₄ CH ₂ Cl	86-95° (3-5 mm)	50-55
p-C ₂ H ₅ OC ₆ H ₄ CH ₂ Cl	108-110 (5-6 mm)	45-50
p-C ₃ H ₇ OC ₆ H ₄ CH ₂ Cl	118-122 (7-9 mm)	50
p-iso-C ₃ H ₇ OC ₆ H ₄ CH ₂ Cl	112-116 (7-8 mm)	50
p-C ₄ H ₉ OC ₆ H ₄ CH ₂ Cl	132-133 (3-5 mm)	68-70
3,4-(OCH ₃) ₂ C ₆ H ₃ CH ₂ Cl	135-145 (10 mm) m. p. 68-71	38

by filtration from resinous admixtures, and a concentrated solution of soda was added to the filtrate until the reaction was alkaline to litmus. The substance which separated was extracted with ether and the ethereal solution was washed with water and dried with sodium sulfate. The ether was driven off and the residue was vacuum distilled. The distilled substance was dissolved in ether and an ethereal solution of hydrogen chloride was gradually added to the solution. The hydrochlorides of the substituted benzyl-N-bis-(chloroethyl)-amines were recrystallized from organic solvents.

SUMMARY

Nucleus-substituted benzyl-N-bis-(chloroethyl)-amines which had not previously been described in the literature were prepared and new data relative to the method of preparing certain of the starting materials were submitted.

LITERATURE CITED

- [1]. E. Wilson and M. Tishler, J. Am. Chem. Soc., 73, 3635 (1951).
- [2]. R. Quelet, Comptés rend., 196, 1411 (1933).
- [3]. K. Schulze, Ber., 17, 1527 (1884); O. Scherler, Ber., 24, 3921 (1891).
- [4]. G. Banse, Ber., 27, 2169 (1894).
- [5]. W. M. Lauer and L. I. Hansen, J. Am. Chem. Soc., 61, 3039 (1939).
- [6]. C. Mettler, Ber., 39, 2937 (1906).

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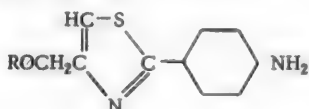


4-ALKOXYMETHYL- AND 4-ARYLOXYMETHYL-2-(p-AMINOPHENYL)-THIAZOLES

S. G. Fridman

In a preceding work [1], the synthesis of 6-aminobenzthiazoles with alkoxy and aryloxymethyl groups in position 2 was described.

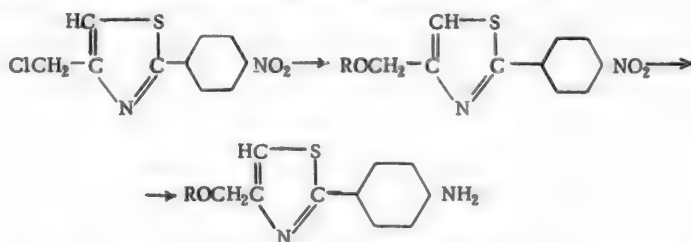
In the present work, the synthesis of similar derivatives of thiazole — the 4-alkoxymethyl- and 4-aryloxymethyl-2-(p-aminophenyl)-thiazoles of the general formula:



are described.

3 Isomeric (p-aminophenyl)-thiazoles [2] are described in the literature, but compounds simultaneously containing the p-aminophenyl and alkoxy or aryloxymethyl radical have not been prepared by anyone up to this time.

The synthesis under consideration was accomplished by the reaction of 4-chloromethyl-2-(p-nitrophenyl)-thiazole with alcoholates and phenolates and subsequent reduction of the ethers of 4-hydroxymethyl-2-(p-nitrophenyl)-thiazole into corresponding amino derivatives in accord with the scheme:



where R = CH₃, C₂H₅, C₃H₇ (n- and iso-), C₄H₉ (n- and iso-), C₅H₁₁ (iso),

C₆H₁₁, C₆H₅, p-ClC₆H₄, o-CH₃OC₆H₄, p-CH₃OC₆H₄, C₆H₅CH₂

The initial 4-chloromethyl-2-(p-nitrophenyl)-thiazole is well known and was prepared by nitrating 4-chloromethyl-2-phenylthiazole [3]. Preliminary experiments showed that, under the conditions which we used for the synthesis of 2-alkoxymethyl-6-nitrobenzthiazoles [1], only sodium methylate and benzylate react with 4-chloromethyl-2-(p-nitrophenyl)-thiazoles with the formation of 4-methoxymethyl- and 4-benzyloxymethyl-2-(p-nitrophenyl)-thiazoles. The action of other alcoholates leads to the formation of high-melting products which were not investigated in greater detail.

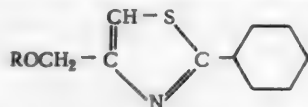
Another method was selected which consisted in initially obtaining the 4-alkoxymethyl-2-phenylthiazoles, which were then nitrated. The 4-alkoxymethyl-2-phenylthiazoles were prepared in excellent yields by heating 4-chloromethyl-2-phenylthiazole with the corresponding alcoholates. They consisted of colorless liquids which formed picrates which crystallized well. The boiling points, yields and analytical results for the 4-alkoxymethyl-2-phenylthiazoles are given in Table 1. All the preparations set forth are new compounds.

By the nitration of 4-alkoxymethyl-2-phenylthiazoles, products were formed, in the molecule of which the nitro group occupies, as one would naturally expect, the para position in the phenyl ring, which was demonstrated by oxidation to p-nitrobenzoic acid. As in the case of nitration of the 2-alkoxymethylbenzthiazoles, we did not succeed in obtaining the normal nitration products under the conditions which we used (sulfuric acid medium), when the alkyl group was branched. 4-Isobutoxymethyl-2-phenylthiazole, which formed 4-isobutoxymethyl-2-(p-nitrophenyl)-thiazole in a 25% yield, was an exception. The nitration of 4-isopropoxymethyl-2-phenylthiazole

led to the formation of a product with a m.p. of 80°, which contained 4% more nitrogen and sulfur than were required. We did not investigate this product in more detail. By nitrating 4-isoamylloxymethyl-2-phenylthiazole, a product with a m.p. of 167-168°, which agreed in its nitrogen and sulfur content with the dealkylation product - 4-hydroxymethyl-2-(p-nitrophenyl)-thiazole, was isolated.

TABLE 1

4-Alkoxyethyl-2-phenylthiazoles of the General Formula:



Sequence No. of the compound	R	B.p. at the given pressure (mm)	Yield (in %)	M.p. of the picrate	Empirical formula	Analytical results	
						Nitrogen (in %)	
						Found	Calculated
I	C ₆ H ₅ -.....	172-174° (12)	82	-	C ₁₂ H ₁₃ ONS*	6.07 6.16	6.39
II	CH ₃ -CH ₂ -CH ₂ -.....	183-185 (12)	71	-	C ₁₃ H ₁₅ ONS	5.75 5.69	6.00
III	CH ₃ \ CH-..... /	165-167 (5)	72	109°	C ₁₉ H ₁₈ O ₈ N ₄ S (picrate)	12.12 12.34	12.12
IV	CH ₃ -CH ₂ -CH ₂ -CH ₂ -...	173-174 (5)	80	-	C ₁₄ H ₁₇ ONS	5.19 5.24	5.67
V	CH ₃ \ CH-CH ₂ -..... /	183-184 (10)	82	85	C ₁₄ H ₁₇ ONS	5.28 5.11	5.67
VI	CH ₃ \ CH-CH ₂ -CH ₂ -... /	179-181 (5)	81	76	C ₁₅ H ₁₉ ONS	5.13 5.14	5.36
VII	CH ₂ \ CH ₂ -CH ₂ \ CH-..... / /	206-208 (5)	70	89	C ₂₂ H ₂₂ O ₈ N ₄ S picrate	11.39 11.41	11.15

The 4-aryloxymethyl-2-(p-nitrophenyl)-thiazoles were prepared with excellent yields by heating 4-chloromethyl-2-(p-nitrophenyl)-thiazole with the corresponding phenols in acetone solution in the presence of anhydrous potash. The preparations of this groups which we obtained are set forth in Table 2. They consisted of substances which crystallized very well. The 4-alkoxymethyl-2-(p-nitrophenyl)-thiazoles were quite soluble in alcohol, and ether, and were poorly soluble in water. They were recrystallized from alcohol. The 4-aryloxymethyl-2-(p-nitrophenyl)-thiazoles were poorly soluble in alcohol; they were therefore recrystallized from glacial acetic acid.

The 4-alkoxymethyl- and 4-aryloxymethyl-2-(p-nitrophenyl)-thiazoles were reduced in an alcohol-water medium by iron filings in the presence of acetic acid. The majority of the amines obtained were isolated in the pure form, and the rest were identified in the form of the hydrochlorides and acetyl derivatives. The amines which were isolated consisted of colorless needles, quite soluble in alcohol and poorly soluble in water. They were recrystallized from aqueous alcohol. The yields, melting points and analytical data for the amines isolated are set forth in Table 3. We did not succeed in isolating the product of the reduction of 4-benzoyloxymethyl-2-(p-nitrophenyl)-thiazole, probably as a consequence of the low stability of the benzoyloxy group.

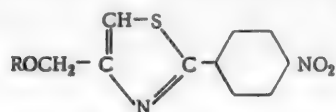
The hydrochlorides of the 4-alkoxymethyl- and 4-aryloxymethyl-2-(p-aminophenyl)-thiazoles consisted of yellow colored needles. The hydrochlorides of the alkoxyethyl-derivatives were quite soluble in water, but hydrolyzed at the same time. The salts were readily diazotized and yielded azo dyes by combination with β-naphthol. The hydrochlorides of 4-aryloxymethyl-2-(p-aminophenyl)-thiazoles were difficultly soluble even in boiling water. They were recrystallized from alcohol. The melting points and analytical data of the hydrochlorides are set forth in Table 4.

The acetyl derivatives of the 4-alkoxymethyl- and 4-aryloxymethyl-2-(p-aminophenyl)-thiazoles were readily obtained in the crystalline form; they were recrystallized from benzene. The diacetyl derivatives were recrystallized from glacial acetic acid.

* Found %: S 14.50, 14.68. Calculated % S 14.60

TABLE 2

4-Alkoxymethyl- and 4-Aryloxymethyl-2-(p-nitrophenyl)-thiazoles of the General Formula:



Sequence No. of the compound	R	M.p.	Yield (in %)	Empirical formula	Analytical results			
					Nitrogen (in %)		Sulfur (in %)	
					Found	Calculated	Found	Calculated
I	CH ₃ -.....	143-144°	80	C ₁₁ H ₁₀ O ₃ N ₂ S	11.23 11.04	11.20	12.67 12.77	12.80
II	CH ₃ -CH ₂ -.....	90-90.5	75	C ₁₂ H ₁₂ O ₃ N ₂ S	10.46 10.57	10.60	12.05 12.15	12.12
III	CH ₃ -CH ₂ -CH ₂ -....	84-84.5	55	C ₁₃ H ₁₄ O ₃ N ₂ S	10.17 10.24	10.07	11.43 11.60	11.51
IV	CH ₃ -CH ₂ -CH ₂ -CH ₂ -	62	50	C ₁₄ H ₁₆ O ₃ N ₂ S	9.80 9.85	9.58	11.02 11.08	10.96
V	CH-CH ₂ -....	49.5-50	25	C ₁₄ H ₁₆ O ₃ N ₂ S	9.59 9.71	9.58	11.05 11.15	10.95
VI	112	70	C ₁₆ H ₁₂ O ₃ N ₂ S	9.01 9.02	8.97	10.17 10.36	10.25
VII	120	80	C ₁₆ H ₁₁ O ₃ N ₂ SCl	8.05 8.20	8.08	10.34 10.41	10.24*
VIII	198	31	C ₁₆ H ₁₁ O ₅ N ₃ S	11.70 11.82	11.76	8.86 9.02	8.96
IX	216-217	15	C ₁₆ H ₁₁ O ₅ N ₃ S	11.51 11.50	11.76	8.88 8.80	8.96
X	152	70	C ₁₇ H ₁₄ O ₄ N ₂ S	8.13 8.31	8.18	9.29 9.40	9.35
XI	109.5-110	64	C ₁₇ H ₁₄ O ₄ N ₂ S	7.98 8.11	8.17	9.36 9.37	9.35
XII	147	60	C ₁₇ H ₁₄ O ₃ N ₂ S	8.81 8.85	8.59	10.06	9.81

The 4-alkoxymethyl- and 4-aryloxymethyl-2-(p-acetylamino-phenyl)-thiazoles consisted of colorless crystals with a melting point above 100°. The melting points and analytical data are presented in Table 5.

EXPERIMENTAL

4-Chloromethyl-2-phenylthiazole was prepared by condensing symmetrical dichloroacetone and thiobenzamide under the conditions described in the literature [3].

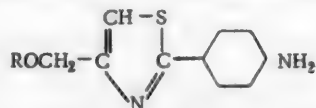
4-Chloromethyl-2-(p-nitrophenyl)-thiazole was also prepared in accordance with the literature data [4], with small changes. 27 g of 4-chloromethyl-2-phenylthiazole was added in portions to 50 ml of concentrated sulfuric acid

* It was analyzed for chlorine content.

while it was being mechanically stirred. The solution obtained was cooled to +5°, and a mixture of 30 ml of nitric acid (d 1.5) in 3) ml of concentrated sulfuric acid was added in the form of drops at this temperature over a period of 30-40 minutes. The reaction mass was stirred at room temperature for 1 hour and then was poured out in a fine stream into a 20% solution of sodium hydroxide (800 ml), which contained 800 g of crushed ice. The precipitate which settled out was filtered off, washed with water, dried in air and recrystallized from alcohol. The yield was 22.5 g (70%). The m.p. was 120°, which was in accord with the literature data.

TABLE 3

4-Alkoxyethyl- and 4-Aryloxyethyl-2-(p-aminophenyl)-thiazoles of the General Formula :



Sequence No. of the compound	R	M.p.	Yield (in %)	Empirical formula	Analytical results			
					Nitrogen (in %)		Sulfur (in %)	
					Found	Calculated	Found	Calculated
I	CH ₃ -.....	77°	65	C ₁₁ H ₁₂ ON ₂ S	12.37 12.46	12.12	14.25	14.54
II	CH ₃ -CH ₂ -CH ₂ -	75	41	C ₁₃ H ₁₆ ON ₂ S	11.45 11.41	11.29	12.94 13.04	12.90
III		85	80	C ₁₄ H ₁₈ ON ₂ S	10.84 10.71	10.68	11.97 12.00	12.21
IV		98	75	C ₁₆ H ₁₄ ON ₂ S	9.70 9.81	9.92	11.05 10.89	11.34
V	CH ₃ O-	144-145	80	C ₁₇ H ₁₆ O ₂ N ₂ S	8.91 9.11	8.98	10.23 10.35	10.25
VI		130-131	60	C ₁₇ H ₁₆ O ₂ N ₂ S	8.83 9.11	8.98	10.26 10.37	10.25
VII	Cl-	119	63	C ₁₆ H ₁₃ ON ₂ SCl	8.91 8.74	8.84	11.11 10.94	11.21

4-Alkoxyethyl-2-phenylthiazoles (I-VII, Table 1). 1). 0.7 g of sodium was dissolved in 20 ml of the appropriate anhydrous alcohol, and a solution of 6.2 g of 4-chloromethyl-2-phenylthiazole in 15 ml of the same alcohol was added to the solution obtained. The mixture was heated on a boiling water bath for 3 hours and the alcohol was then driven off in a vacuum, the residue was stirred into 20 ml of water and extracted with ether. The ethereal solution was dried with roasted sodium sulfate and, after driving off the ether, the residue was vacuum distilled. We did not succeed in obtaining a few of the compounds (V, VI) in the analytically pure form. The picrates were obtained in an alcoholic solution and recrystallized from alcohol.

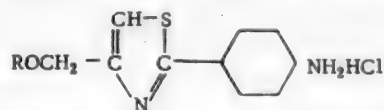
Nitration of 4-ethoxymethyl-2-phenylthiazole. 6.6 g of 4-ethoxymethyl-2-phenylthiazole was added to 15 ml of concentrated sulfuric acid which was being cooled and mechanically stirred, and the solution obtained was cooled to -1 to -2°. At this temperature, a mixture of 7 ml of nitric acid (d 1.5) in 10 ml of concentrated sulfuric acid was added in the form of drops over a period of 30 minutes. The reaction mixture was stirred for 30 minutes more and then poured out into a 20% solution of sodium hydroxide (160 ml), containing 300 g of crushed ice. The precipitate which settled out was filtered off, washed, dried in air, and recrystallized from alcohol. The yield of recrystallized product was 6 g (75%). The m.p. was 90°.

Preparations III, IV and V (Table 2) were prepared analogously.

4-Methoxymethyl-2-(p-nitrophenyl)-thiazole (I) and 4-benzyloxymethyl-2-(p-nitrophenyl)-thiazole (XII) were prepared by the reaction of 4-chloromethyl-2-(p-nitrophenyl)-thiazole with sodium methylate and sodium benzyolate analogously to the 4-alkoxyethyl-2-phenylthiazoles.

TABLE 4

Hydrochlorides of 4-Alkoxyethyl- and 4-Aryloxyethyl-2-(p-aminophenyl)-thiazoles of the General Formula:



Sequence No. of the compound	R	M.p.	Empirical formula	Analytical results	
				Nitrogen (in %)	
				Found	Calculated
I	CH ₃ -	185-186° (with decomp.)	C ₁₁ H ₁₃ ON ₂ SCl	9.77 9.69	10.87
II	CH ₃ -CH ₂ -	Hygroscopic	—	—	—
III	CH ₃ -CH ₂ -CH ₂ - ..	181-182 (with decomp.)	C ₁₃ H ₁₇ ON ₂ SCl	9.89 9.96	9.84
IV	CH ₃ -CH ₂ -CH ₂ -CH ₂ - ..	185-187 (with decomp.)	C ₁₄ H ₁₉ ON ₂ SCl	9.10 9.13	9.88
V		187 (with decomp.)	C ₁₄ H ₁₉ ON ₂ SCl	9.54 9.37	9.38
VI		186-187	C ₁₆ H ₁₅ ON ₂ SCl	8.75 8.84	8.78
VII		215-216 (with decomp.)	C ₁₆ H ₁₄ ON ₂ SCl ₂	7.85 8.01	7.98
VIII	HCl · NH ₂ ·	230-235 (with decomp.)	C ₁₆ H ₁₇ ON ₃ SCl ₂	11.07 10.94	11.35
IX		222-223 (with decomp.)	C ₁₆ H ₁₇ ON ₃ SCl ₂	11.30	11.35
X	CH ₃ O-	197 (with decomp.)	C ₁₇ H ₁₇ O ₂ N ₂ SCl	7.78 7.68	8.03
XI		180 (with decomp.)	C ₁₇ H ₁₇ O ₂ N ₂ SCl	7.97 7.79	8.03

A product with a m.p. of 80° was obtained by nitrating 4-isopropoxymethyl-2-phenylthiazole. Analysis of this product showed an increased nitrogen and sulfur content.

Found %: N 14.32; 14.14; S 16.44; 4-Isopropoxy-2-(p-nitrophenyl)-thiazole. Calculated %: N 10.07; S 11.51.

We have still not elucidated of what the product isolated consists.

The nitration of 4-isopropoxy-2-phenylthiazole under the same conditions led to the formation of a product with a m.p. of 169-170°, which, agreed in its analytical data with those of 4-hydroxymethyl-2-(p-nitrophenyl)-thiazole.

Found %: N 11.66; 11.84; S 13.46. C₁₆H₁₅O₃N₂S. Calculated %: N 11.76; S 13.44.

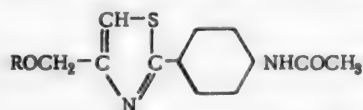
We did not succeed in isolating the product of the nitration of 4-cyclohexyloxymethyl-2-phenylthiazole.

Position of the nitrogroup in the nitration products of the 4-alkoxyethyl-2-phenylthiazoles. 0.5 g of the nitrophenylthiazole derivative was added to a solution of 5 g of potassium bichromate in a mixture of 20 ml of concentrated sulfuric acid and 15 ml of water, and the mixture was boiled moderately for 1 hour. After cooling, 50 ml of water was added and the white precipitate which settled out was filtered off, washed with water and

dried. The m.p. was 238°; the substance displayed no melting point depression in a mixed sample with p-nitrobenzoic acid. The yield of p-nitrobenzoic acid amounted on the average to around 70%.

TABLE 5

Acetyl Derivatives of 4-Alkoxymethyl- and 4-Aryloxymethyl-2-(p-aminophenyl)-thiazoles of the General Formula:



Sequence number of the compound	R	M.p.	Empirical formula	Analytical results	
				Nitrogen (in %)	
				Found	Calculated
I	CH ₃ -.....	121°	C ₁₃ H ₁₄ O ₂ N ₂ S	10.58 10.63	10.67
II	CH ₃ -CH ₂ -....	150	C ₁₄ H ₁₆ O ₂ N ₂ S	10.07 9.90	10.14
III	CH ₃ -CH ₂ -CH ₂ -	146-147	C ₁₅ H ₁₈ O ₂ N ₂ S	9.70 9.69	9.65
IV	CH ₃ -CH ₂ -CH ₂ -CH ₂ -	101-102	C ₁₆ H ₂₀ O ₂ N ₂ S	9.39 9.22	9.21
V		109-110	C ₁₆ H ₂₀ O ₂ N ₂ S	9.23 9.03	9.21
VI		141-142	C ₁₈ H ₁₈ O ₂ N ₂ S	8.54 8.72	8.64
VII		171	C ₁₈ H ₁₅ O ₂ N ₂ SCl	7.79 7.69	7.81
VIII	CH ₃ CONH	259	C ₂₀ H ₁₉ O ₃ N ₃ S	11.07 11.11	11.02
IX		217	C ₂₀ H ₁₉ O ₃ N ₃ S	10.50	11.02
X	CH ₃ O-	170-171	C ₁₉ H ₁₈ O ₃ N ₂ S	7.80 7.97	7.90
XI		161-161.5	C ₁₉ H ₁₈ O ₃ N ₂ S	7.64 7.61	7.90

4-Aryloxymethyl-2-(p-nitrophenyl)-thiazoles. A mixture, consisting of 2.5 g (0.01 mole) of 4-chloromethyl-2-phenylthiazole, 0.02 mole of the corresponding phenol, 2.7 g (0.02 mole) of anhydrous potash and 75 ml of dry acetone, was boiled on a water bath for 24-25 hours. After distilling off the acetone, the residue was stirred into water, filtered, washed with a 5% solution of sodium hydroxide, then with water, and after drying, was recrystallized from glacial acetic acid. The data for the preparations obtained are set forth in Table 2 (VI-XII).

Reduction of 4-alkoxymethyl- and 4-aryloxymethyl-2-(p-nitrophenyl)-thiazoles. 10 ml of 20% acetic acid was added to a solution or a suspension of 0.01 mole of the nitrophenyl derivative of thiazole in 50 ml of alcohol; the reduction was carried out with iron filings, just as in the reduction of the 2-alkoxymethyl- and 2-aryloxymethyl-6-nitrobenzthiazoles. The amines isolated in the crystalline form are presented in Table 3. They consisted of colorless crystals. Alcoholic and ethereal solutions fluoresced with a beautiful violet color. The liquid amines were extracted with ether, the ethereal solution was washed with sodium bicarbonate and dried with anhydrous sodium sulfate. After distilling off the ether, the residue was identified in the form of the hydrochloride and the acetyl derivative.

The hydrochlorides of the 4-alkoxymethyl- and 4-aryloxymethyl-2-(p-aminophenyl)-thiazoles were prepared

by mixing an alcoholic solution of the amine with an ethereal solution of hydrogen chloride. The precipitate of the salt which settled out was recrystallized from alcohol.

The acetyl derivatives were prepared by briefly boiling the amine with acetic anhydride. The monoacetyl derivatives were recrystallized from benzene and the diacetyl derivatives from glacial acetic acid.

SUMMARY

1. A number of 4-alkoxymethyl-2-phenylthiazoles were prepared; the corresponding p-nitrophenyl derivatives were obtained by nitrating them.

2. The corresponding aryloxy derivatives were prepared from 4-chloromethyl-2-(p-nitrophenyl)-thiazole by reaction with phenols.

3. The corresponding amines were prepared by reducing the 4-alkoxymethyl- and 4-aryloxymethyl-2-(p-nitrophenyl)-thiazoles.

LITERATURE CITED

- [1]. S. G. Fridman, J. Gen. Chem., 24, 642 (1954). *
- [2]. H. Erlenmeyer, J. Eckenstein, E. Sorkin, H. Meyer, Helv. Chim. Acta, 33, 1271 (1950).
- [3]. C. Suter, T. Johnson, Rec. trav. chim., 49, 1066 (1930); F. Hooper, T. Johnson, J. Am. Chem. Soc., 56, 470, 485 (1934).
- [4]. B. Friedman, M. Sparks, R. Adams, J. Am. Chem. Soc., 59, 2262 (1937).

* Consultant's Bureau Translation, p. 651.

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SYNTHESES BASED ON ANABASINE

VII. SULFONATION OF ANABASINE BY PYRIDINESULFOTRIOXIDE

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Our preceding work [1] was devoted to the study of the amination of anabasine, N-methylanabasine and nicotine by sodium amide in the absence of solvents. In the present article, the results of the sulfonation of anabasine, piperidine and certain of their derivatives by pyridinesulfotrioxide are reported.

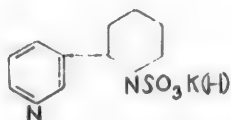
It is well known from the literature data that pyridinesulfotrioxide [2,4] is used for preparing sulfonic acids with the sulfo group located on a carbon atom, and of the so-called sulfamic acids (with the sulfo group at the nitrogen atom) [4-7].

We used this reagent to sulfonate anabasine with the object of synthesizing a sulfamic acid based on the imine group of the piperidine ring. The reaction was conducted under the conditions for sulfonating piperidine [8,9] — at 0° in an aqueous medium in the presence of potash. The sulfamic acid of anabasine was isolated in the form of the potassium salt with a yield of 51.1%. The potassium salt, after recrystallization from alcohol, consisted of colorless crystals with a m.p. of 212-213° and, according to the analysis, contained one sulfo group.

By mixing alcoholic solutions of the potassium salt and picric acid, a picrate was obtained which was identical with anabasine picrate. The dry distillation of a mixture of the potassium salt of the sulfamic acid of anabasine with potassium cyanide yielded anabasine. This indicated the great lability and ready cleavability of the sulfo group.

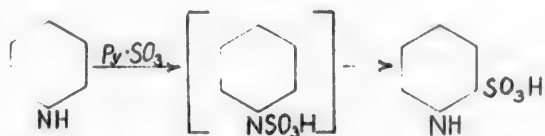
An attempt was made to isolate the sulfamic acid from the potassium salt via heating it with an equimolecular quantity of hydrogen chloride (in alcohol). An oil was thereby obtained, which, in contrast to anabasine, did not dissolve in acetone. It did not crystallize during prolonged standing in a desiccator. We succeeded in recovering the potassium salt from the oil, but in an insignificant yield (12%). Evidently, it was not an individual product, but consisted of a mixture of the sulfamic acid and anabasine sulfate. This permits us to conclude that the sulfamic acid of anabasine is unstable in the free form.

The potassium salt was completely hydrolyzed by a brief heating with 2% hydrochloric acid solution in the presence of barium chloride, and a precipitate of barium sulfate settled out at the same time. Sulfamic acids behave in this way during hydrolysis [5-8]. This gives us the right to assume that the sulfamic acid obtained, which was characterized in the form of the potassium salt, was the sulfamic acid of anabasine:



This is all the more probable since N-methyl- and N-acetylanabasine do not yield the corresponding acids with pyridinesulfotrioxide under similar conditions.

It is of interest to note that, under analogous conditions, Rubtsov, completely unexpectedly, as the author reports, succeeded in obtaining 2-piperidinesulfonic acid from piperidine [8]. Our attempt to obtain the corresponding acids from N-methyl- and N-acetylpiperidine gave negative results. This fact indicates that, in the sulfonation of piperidine, sulfamic acid is apparently formed initially, and then isomerizes into 2-piperidine-sulfonic acid:



Paal and Hubaleck indicate that sulfamic acid is readily hydrolyzed, and the authors consider that, even when the salt of the sulfamic acid of piperidine is stored, partial isomerization occurs. We did not observe such properties in the salt of the sulfamic acid of anabasine.

The experiments which were carried out show that the nitrogen of the piperidine ring of anabasine more strongly retains a sulfo group near it. The pyridine ring in anabasine definitely influences this.

Sulfonation of anabasine with pyridinesulfotrioxide at room temperature permitted the sulfamic acid to be obtained in a considerably smaller yield (15%), while when the reaction was carried out by heating the mixture at 100°, the acid was not obtained at all.

The reaction of anabasine with pyridinesulfotrioxide involving the direct reaction of these compounds was also studied. Experiments involving heating mixtures of the reagents, taken in various molar ratios, at 100 and 150° for 10-15 hours, did not permit us to isolate the crystalline products in appreciable quantities. The reaction was not carried out above 150°, since it is known from the literature data that at 200°, pyridinesulfotrioxide is itself isomerized into the β -sulfonic acid of pyridine [11].

EXPERIMENTAL

We prepared pyridinesulfotrioxide by the method of Terentyev [6].

Sulfonation of anabasine with pyridinesulfotrioxide at 0°. 40 g of ice and 5 g of pyridinesulfotrioxide were added to a solution of 5 g of anabasine in 25 ml of water. The mixture was stirred for 20 minutes. 4.2 g of potash in 6 ml of water was then added to the mixture and the stirring was continued for 35 minutes while the mixture was cooled with ice water. After this, the solution was concentrated to dryness on a water bath. The residue was treated with anhydrous alcohol while being heated. After distilling off the alcohol, 4.4 g (51.1%) of the potassium salt of the sulfamic acid of anabasine was obtained, which had a m.p. of 212-213° after recrystallization from alcohol.

0.09683, 0.10148 g substance; 0.03171, 0.03083 g K_2SO_4 . Found %: K 14.49, 13.48. $C_{10}H_{13}N_2SO_3K$. Calculated %: K 13.93.

Picrate. Upon stirring alcoholic solutions of the potassium salt of the sulfamic acid of anabasine and picric acid, the picrate with a m.p. of 196-197° precipitated. A mixed sample with anabasine picrate melted at 197-198°.

Isolation of the sulfamic acid of anabasine from the potassium salt. An equimolecular quantity of an alcoholic solution of hydrogen chloride (0.065 g) was added to 0.5 g of the potassium salt in anhydrous alcohol. The precipitate of potassium chloride which settled out upon negligible heating was separated and the filtrate concentrated. The residue consisted of an oil which was insoluble in acetone. The oil did not crystallize upon prolonged standing in a desiccator. It yielded a picrate with a m.p. of 198-200° with picric acid. A mixed sample with anabasine picrate melted at 197-200°. Excess 50% potash solution was added to 0.85 g of the oil. The solution was concentrated to dryness. The residue was extracted with anhydrous alcohol. 0.12 g (12%) of the potassium salt with a m.p. of 209-210° was obtained. A mixed sample with the potassium salt of the sulfamic acid of anabasine melted at 209-211°.

Hydrolysis of the potassium salt of the sulfamic acid of anabasine. A small quantity of barium chloride was added to a solution of 0.1702 g of the potassium salt of the sulfamic acid of anabasine in 2% hydrochloric acid. A precipitate of barium sulfate settled out upon negligible heating. A picrate with a m.p. of 196-197° was obtained from the aqueous solution after separating the barium sulfate. A mixed sample with anabasine picrate melted at 196-198°.

SUMMARY

1. The study of the sulfonating action of pyridinesulfotrioxide under various conditions showed that the sulfamic acid can be prepared from anabasine with the aid of this substance.

2. N-Methyl- and N-acetylanabasine, and also the corresponding derivatives of piperidine do not react with pyridinesulfotrioxide under the conditions which permit the preparation of 2-piperidinesulfonic acid.

LITERATURE CITED

- [1] A. S. Sadykov, O. S. Otroshchenko and M. K. Yusupov, *J. Gen. Chem.*, 23, 980 (1953). •
- [2] L. Wagner, *Ber.*, 19, 1157 (1886).
- [3] A. Burg, *J. Am. Chem. Soc.*, 65, 1629 (1943).
- [4] P. Baumgarten, *Ber.*, 57, 1623 (1924); 59, 1166 (1926); 59, 1976 (1926).
- [5] V. N. Ufilmtsev, *J. Gen. Chem.*, 10, 1757 (1940).
- [6] A. P. Terentyev, *Herald of Moscow State University*, 6, 9 (1947).
- [7] A. P. Terentyev and L. V. Tsymbal, *Proc. Acad. Sci. USSR*, 55, 845 (1947).
- [8] M. V. Rubtsov, *Proc. Acad. Sci. USSR*, 79, 267 (1951).
- [9] A. S. Sadykov and O. S. Otroshchenko, *Proc. Acad. Sci. Uzbek. SSR*, No. 7, 23 (1951).
- [10] C. Paal and M. Hubaleck, *Ber.*, 34, 2757 (1901).
- [11] S. McElwain, Goese, *J. Am. Chem. Soc.*, 65, 2233 (1943).

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AN ALKALOID FROM GLEDITSCHIA TRIACANTHOS L.

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Gleditschia triacanthos L. (fam. Caesalpiniaceae) [the honey locust], is a tree with sharp branched thorns, pinnate leaves and fine greenish-white flowers. It is cultivated in the Caucasus, in Central Asia and in the Crimea for decorative purposes [1].

The leaves and fruit of the honey locust contain 100-400 mg% of ascorbic acid [2], and in the pods are found saponins [3], glucosides [4] and the flavonoid pigments acrammerin [5] and olmelin [6,7].

In 1947-1948 one of the authors of this article (M. V. Tsarev) established that the leaves and flowers of the honey locust contain a considerable quantity of alkaloids and that smaller quantities of alkaloids are found in the thorns, bark and seeds. The young, just-opened leaves are richest in alkaloids - to 1% of the air-dry weight. As the leaf grows, the alkaloid content sharply falls; leaves collected in July contain only traces of alkaloids. The flowers of the honey locust contain 0.3%, and the seeds 0.05% of alkaloids.

A crystalline alkaloid with a m.p. of 227-228°, named triacanthine, was isolated in 1949 from the young leaves of the honey locust.

Our investigations have established that the composition of triacanthine corresponds with the formula $C_8H_{10}N_4$.

Triacanthine crystallizes from alcohol in the form of white rhombic crystals. It is quite soluble in alcohol, more difficultly soluble in chloroform and almost insoluble in water and ether.

Triacanthine is a strong base and is precipitated out from solutions of its salts by strong alkalis. It reduces potassium permanganate at any pH value and is readily oxidized by bromine and chromic acid. Triacanthine forms well crystallized salts with mineral and organic acids: the hydrochloride has a m.p. of 218-219°, the nitrate, a m.p. of 164-166°, the hydrobromide, a m.p. of 215-216°, the picrate, a m.p. of 239-241°, the picrolonate, a m.p. of 229-231° and the sulfates, m.p. of 175-176° and 216-217°. The hydrochloride, the hydrobromide, the nitrate and the sulfates are quite soluble in water and alcohol; the picrate and the picrolonate are insoluble in water and difficultly soluble in alcohol. The iodomethylate of triacanthine consists of white flakes or needles which melt at a temperature of 199-203°. The iodomethylate is insoluble in water, dissolves readily in methyl alcohol and more poorly in ethyl alcohol.

The composition and properties of triacanthine and the melting points of its salts and of the iodomethylate provide a basis for assuming that it is a new alkaloid which has not previously been described in the literature.

EXPERIMENTAL

1. Isolation and Purification of the Alkaloid

Pulverized air-dry leaves of the honey locust were moistened with 10% aqueous ammonia solution and exhaustively extracted with dichloroethane. The extract obtained was treated several times with 5% sulfuric acid until the alkaloids were completely extracted, after which the sulfuric acid solution of triacanthine was rendered alkaline with 50% sodium hydroxide solution and the precipitate which fell out of triacanthine base was filtered off. The triacanthine which was left in the solution was extracted with chloroform, the chloroform solution was dried with anhydrous sodium sulfate, filtered off, (and the solvent driven off and the solution concentrated to dryness on a water bath.

The triacanthine isolated was dissolved in 5% sulfuric acid, the sulfuric acid solution was rendered alkaline with 50% sodium hydroxide solution, and the alkaloid extracted with chloroform. After drying the solution, the chloroform was driven off, and the triacanthine twice recrystallized from alcohol. 100 g of pure triacanthine which melted at 227-228° was obtained from 20 kg of leaves.

* Deceased

The triacanthine was subjected to further purification for conducting the elementary analysis for carbon, hydrogen and nitrogen by the methods of Liebig and Dumas. Sulfuric acid (d 1.84) was added in the form of drops to a solution of 0.5 g of triacanthine in 5 ml of alcohol until the reaction was acid to litmus. The sulfate which precipitated was filtered off, recrystallized from alcohol, dissolved in 5 ml of water, rendered alkaline with 30% sodium hydroxide solution, and isolated in the form of triacanthine base by two-fold recrystallization from alcohol. After drying in a vacuum-pistol at 100° for 14 hours, the triacanthine melted at 228°.

4.760 mg substance: 10.336 mg CO₂; 2.683 mg H₂O. 3.860 mg substance: 8.389 mg CO₂; 2.178 mg H₂O. 3.120 mg substance: 0.960 ml N₂ (22°, 735 mm). 3.550 mg substance: 1.092 ml N₂ (22°, 735 mm). Found %: C 59.26, 59.31; H 6.30, 6.31; N 34.46, 34.73. C₈H₁₈N₄. Calculated %: C 59.23; H 6.21; N 34.54.

0.0106 g substance; 0.2304 g camphor: Δt 12°. 0.0188 g substance; 0.2528 g camphor: Δt 11°. Found: M 153.36, 169.63. C₈H₁₈N₄. Calculated: M 162.19.

The triacanthine picrate, prepared by stirring alcoholic solutions of triacanthine-base and picric acid together, and recrystallization from alcohol, melted at 239-241°.

4.560 mg substance: 7.448 mg CO₂; 1.521 mg H₂O. 2.078 mg substance: 3.68 mg 0.01 N H₂SO₄. 4.812 mg substance: 8.48 mg 0.01 N H₂SO₄. Found %: C 44.57; H 3.73; N 24.80. 24.67. C₈H₁₈N₄ · C₆H₃O₇N₃. Calculated %: C 42.97; H 3.35; N 25.06

0.0106 g substance: 0.2502 g camphor: Δt 4.5°. Found: M 376.53. C₈H₁₈N₄ · C₆H₃O₇N₃. Calculated: M 391.30.

2. Preparation of the Derivatives

a) A solution of 0.2 g of triacanthine in 5 ml of alcohol was saturated with dry hydrogen chloride. The hydrochloride precipitated in the form of fine white needles, and, after recrystallization from alcohol, melted at 218-219°.

b) Hydrobromic acid (d 1.51) was added in the form of drops to a solution of 0.2 g of triacanthine in 5 ml of alcohol until a precipitate began to appear. After recrystallization from alcohol, the triacanthine hydrobromide had the form of flat white needles which melted at 215-216°.

c) Upon adding nitric acid (d 1.39) in the form of drops to an alcoholic solution of triacanthine, and subsequent cooling for an hour at 0°, lamellar crystals of triacanthine nitrate precipitated. After recrystallization from alcohol, the nitrate had a m.p. of 164-166 and was hygroscopic.

d) The picrolonate of triacanthine was prepared by stirring a solution of 0.2 g of triacanthine in 5 ml of alcohol with 5 ml of an alcoholic solution of picrolonic acid. It crystallized from alcohol in the form of very fine yellow crystals, m.p. 229-231°.

e) The crystalline sulfates, with m.p. 175-176° and 216-217°, were prepared by adding various quantities of sulfuric acid (d 1.84) to an alcoholic solution of triacanthine.

f) 2 ml of methyl iodide was added to a solution of 0.1 g of triacanthine in 5 ml of methyl alcohol and the mixture was heated with a reflux condenser on a water bath for 3 hours, after which the iodomethylate was filtered off and recrystallized from alcohol three times. The m.p. was 199-203°.

The chemical study of triacanthine is being continued.

SUMMARY

1. The new alkaloid triacanthine, with composition C₈H₁₈N₄, was isolated from the leaves of *Gleditschia triacanthos* L. [The honey locust]

2. The following derivatives of triacanthine were prepared and characterized: the hydrochloride, hydrobromide, nitrate, picrate, picrolonate, the sulfates and the iodomethylate.

LITERATURE CITED

- [1] L. A. Kursanov, N. A. Komarnitsky and others. Botany. Moscow, Pt. II. 229-231 (1951).
- [2] A. A. Grossheim, Plant Wealth of the Caucasus, Moscow, 250 (1952).
- [3] C. Wehmer. The Composition of Plants. Jena, V. 1, 508 (1929).

- [4] A. M. Gakhokidze, J. Appl. Chem., 19, 1197 (1946).
- [5] A. M. Gakhokidze and N. D. Kutidze, J. Appl. Chem., 20, 899 (1947).
- [6] A. M. Gakhokidze, J. Appl. Chem., 23, 747 (1950).*
- [7] A. M. Gakhokidze, J. Appl. Chem., 23, 559 (1950).*

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Aromatic Plant Institute

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- * Consultant's Bureau Translation; p. 789.
 - ** Consultant's Bureau Translation; p. 589.

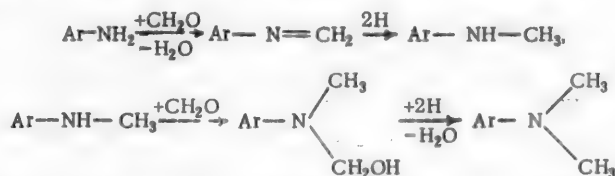


THE DIMETHYLATION OF PRIMARY AROMATIC AMINES WITH THE AID OF FORMALDEHYDE. PREPARATION OF 4-NITRODIMETHYLANILINE

B. M. Bogoslovsky

The possibility of methylating amines via their reaction with a mixture of formaldehyde and formic acid, which can be considered as a special case of the widely known Leuckart reaction, has been repeatedly mentioned in the literature. At the same time, however, it must be emphasized that in the overwhelming majority of cases the indicated method of methylation was used only in relation to primary amines and also to α - and β -amino acids of the aliphatic series. It has been applied more rarely to amines of the alicyclic series and still more rarely to heterocyclic amines. One of the few examples of the application of the reaction under consideration to amines of the aromatic series is the conversion of 2,4,6-tribromoaniline into 2,4,6-tribromodimethylaniline [1,2].

The mechanism of the case of methylation of aromatic amines under consideration does not appear to have been studied in detail. In all probability, the process occurs in stages; the monomethyl derivatives are initially formed [3], and these are then converted into the dimethyl derivatives by the following probable scheme:



In both cases, the reducing agent is formic acid, the reducing capacity of which has been repeatedly referred to by many authors.

The comparatively limited application of the possibility of dimethylating primary aromatic amines, evidently, can be explained by their tendency to form the corresponding diarylmethane derivatives by reaction with formaldehyde. The latter direction of the reaction can prove to be competitive, while it sometimes prevails in the case of the conversion under consideration. Thus, in particular, in the case of the methylation of α -amino-pyridine, described by Chichababin and Knunyants, tetramethyl derivatives of diaminodipyridylmethane [4] are finally formed. According to the investigation of Titov and Baryshnikova, this reaction proceeds in stages, to wit: dimethylamino-pyridine is formed first and then dimethylaminopyridylcarbinol is formed which, condensing with a second molecule of dimethylaminopyridine, forms the end product—the corresponding dipyridylmethane derivative [5].

If one considers what has been set forth above, it becomes clear that dimethylation in accord with the Leuckart method can have a chance of success only for those aromatic amines in the molecule of which some substituent that inhibits the formation of the diarylmethane derivative is found in the para position to the amino group. Thus, of the three isomeric nitroanilines, only 4-nitroaniline fulfills the set condition; consequently, only when this latter compound is used can the formation of the dimethylated derivative in good yields be expected. It should be noted, incidentally, that the methods for preparing 4-nitrodimethylaniline described in the literature are characterized by comparatively low yields and are often accompanied by the necessity of separating the mixture of amines which is formed; 2- and 3-nitroanilines, with the para position to the amino group unsubstituted, can also form the corresponding diphenylmethane derivatives.

The experiments confirmed the assumptions made above. Actually, 4-nitroaniline was successfully converted into 4-nitrodimethylaniline in very excellent yields. 3-Nitroaniline was converted into 2,2'-dinitro-4,4'-bis-(dimethylamino)-diphenylmethane in equally good yields, while for the case of 2-nitroaniline, we succeeded in making secure the preparation of the corresponding diaminodinitrodiphenylmethane, which evidently underwent further methylation with great difficulty under the conditions which we employed.

EXPERIMENTAL •

1. Reaction of 4-Nitroaniline with Formaldehyde. Preparation of 4-Nitrodimethylaniline

20 g of 4-nitroaniline was dissolved by heating in 45 ml of 100% HCOOH, after which 45 ml of a 30% solution of formaldehyde together with 5 g of paraformaldehyde was added to the transparent solution which was formed. After heating for 30 minutes on a water bath, which was accompanied by the evolution of gas bubbles from the reaction mass, the contents of the flask with the abundant yellow precipitate which was formed, were cooled, the liquid was drawn off, and the precipitate washed with water and dried. The yield of product with a m.p. of 148° amounted to 20 g. After crystallization from glacial acetic acid, 16 g (87%) of 4-nitrodimethylaniline was obtained in the form of bright yellow crystals with a m.p. of 161-163°. A mixed sample with the pure product, prepared by oxidizing 4-nitrosodimethylaniline and which had a m.p. of 162-163°, displayed no melting point depression.

2. Reaction of 3-Nitroaniline with Formaldehyde. Preparation of 2,2'-Dinitro-4,4'-tetramethyldiaminodiphenylmethane

45 ml of a 30% formaldehyde solution with 5 g of paraformaldehyde was added to a heated solution of 20 g of 3-nitroaniline in 45 ml of 100% HCOOH, after which the mixture was heated for 2.5 hours on a water bath. The reaction product which was isolated in the precipitate was filtered off, washed with water and dried. The yield of product which had a m.p. of 188°, amounted to 20.2 g. After crystallization from glacial acetic acid, 17 g (about 70%) of 2,2'-dinitro-4,4'-tetramethyldiaminodiphenylmethane was obtained in the form of orange-red crystals with a m.p. of 193° which closely agreed with the literature data. The product obtained displayed no melting point depression in a mixed sample with the pure substance. The diazo reaction did not disclose the presence of amino groups.

3. Reaction of 2-Nitroaniline with Formaldehyde. Preparation of 3,3'-Dinitro-4,4'-diaminodiphenylmethane

The reaction with 2-nitroaniline, conducted under the conditions described above and with the same quantitative relations, led to the formation (after analogous treatment and crystallization from glacial acetic acid) of a substance in the form of orange-red needles with a m.p. of 222-224°. The product obtained had a distinct diazo reaction and closely agreed in its properties (color, melting point) with those of 3,3'-dinitro-4,4'-diaminodiphenylmethane.

SUMMARY

The reciprocal reaction of the three isomeric nitroanilines with formaldehyde in a 100% formic acid medium was studied. It was shown that it is possible to obtain the following with excellent yields: 4-nitrodimethylaniline, 2,2'-dinitro-4,4'-tetramethyldiaminodiphenylmethane and 3,3'-dinitro-4,4'-diaminodiphenylmethane.

LITERATURE CITED

- [1] Clark, Giellespie and Weiss Haus, J. Am. Chem. Soc., 55, 4571 (1933).
- [2] Emerson, Dorf and Deutschmen, J. Am. Chem. Soc., 62, 2159 (1940).
- [3] N. N. Vorozhtsov, Fundamentals of the Synthesis of Intermediate Products and Dyes. State Chem. Press, 537 (1950).
- [4] A. E. Chichababin and I. L. Knunyants, Ber., 62, 3048 (1929).
- [5] A. I. Titov and A. N. Baryshnikova, J. Gen. Chem., 23, 290 (1953). ••

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Moscow Textile Institute

•The student Bolgova participated in the experimental work.

•• Consultant's Bureau Translation, p. 303.

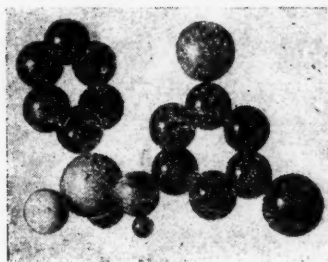


Fig. 2.

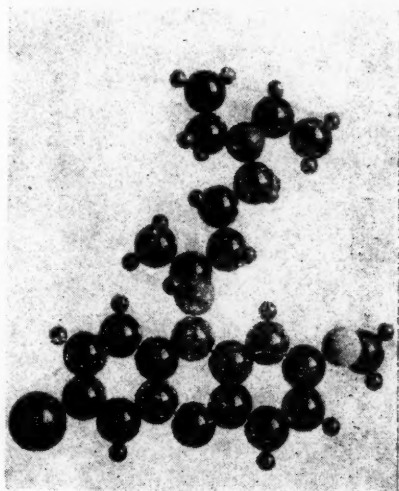


Fig. 1.

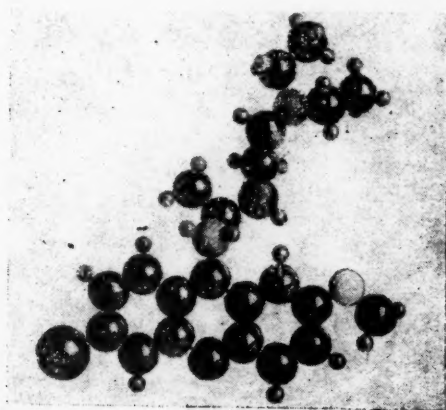


Fig. 2.

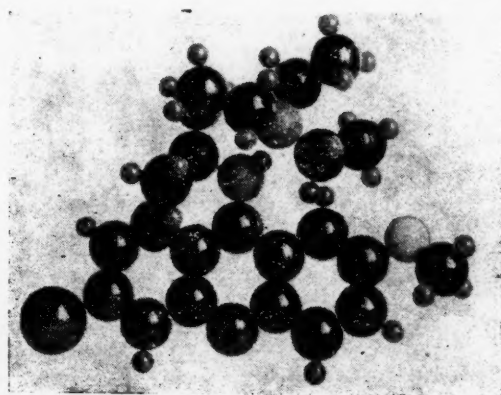


Fig. 4.

